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14. ABSTRACT The LC MURI has pioneered advances in molecular design and synthesis, LC physics and device technology in liquid crystals ranging from main-chain polymers to LC-based NLO materials. Collaboration among seven universities, as well as DoD and industrial labs, achieved ambitious goals that include comprehensive understanding of the role of chain flexibility in governing the orientational order in the solid state of high performance LC plastics (Northwestern/Caltech/Cornell/MIT/BP-Amoco/AFRL collaboration) and solving the mechanism of "V-shaped switching" observed in certain ferroelectric LCs (Colorado/Kent collaboration). Furthermore, interactions under the LC MURI led to important outcomes that were unanticipated at the inception of the center, including the development of materials for high-fidelity 3D microfabrication by 2-photon initiated polymerization (Arizona/Cornell/AFRL collaboration) and the synthesis of new discotic LCs to serve as organic electron conductors for OLED and other applications (Arizona/Colorado/Caltech/Cornell collaboration). Discoveries have been transitioned to DoD labs and industry for technologies including light valves, optical limiters, beam steering devices and information displays.

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**Cumulative Report  
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**Alignment and Packing Behavior of Liquid Crystals and Liquid Crystalline Polymers and  
Their Effects on Optical and Mechanical Properties**

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## **Summary of Effort**

The LC MURI has pioneered advances in molecular design and synthesis, LC physics and device technology in liquid crystals ranging from main-chain polymers to LC-based NLO materials. Collaboration among seven universities, as well as DoD and industrial labs, achieved ambitious goals that include comprehensive understanding of the role of chain flexibility in governing the orientational order in the solid state of high performance LC plastics (Northwestern/Caltech/Cornell/MIT/BP-Amoco/AFRL collaboration) and solving the mechanism of "V-shaped switching" observed in certain ferroelectric LCs (Colorado/Kent collaboration). Furthermore, interactions under the LC MURI led to important outcomes that were unanticipated at the inception of the center, including the development of materials for high-fidelity 3D microfabrication by 2-photon initiated polymerization (Arizona/Cornell/AFRL collaboration) and the synthesis of new discotic LCs to serve as organic electron conductors for OLED and other applications (Arizona/Colorado/Caltech/Cornell collaboration). Discoveries have been transitioned to DoD labs and industry for technologies including light valves, optical limiters, beam steering devices and information displays.

## **I. Structural Liquid-Crystalline Polymers Thrust**

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Julie Kornfield, California Institute of Technology

Christopher Ober, Cornell University

Robert Grubbs, California Institute of Technology

Ned Thomas, Massachusetts Institute of Technology

### **A. Overview of Thrust**

The Structural LCP thrust has assembled a team with diverse expertise and unique synthetic and characterization capabilities to deepen our understanding of main-chain LCPs, which have promise as high performance structural materials. The high strength and stiffness of LCPs is intimately related to their high local degree of molecular orientation, and is strongly impacted by the way in which flow fields during processing couple to the overall molecular orientation state. These processes are complicated by the prevalence of orientational defects in LCPs that result in a ‘polydomain’ texture. We have sought to obtain fundamental, molecular-level insights into the factors that ultimately affect LCP properties through an integrated hierarchy of experiments:

1. Synthesis & scale-up
2. Fundamental molecular and liquid crystalline characteristics
3. Orientation development, texture & rheology in shear flow
4. Towards processing: Orientation development in complex flows

In broadly studying these issues in main-chain LCPs, the thrust has distributed these efforts among materials that fall into three classes:

1. Model materials (well-suited for fundamental studies)
2. ‘Bridge’ materials (special grades or formulations from industrial partners to fill gap between model & commercial LCPs)
3. Commercial LCPs

The following Table illustrates the scope of research that has been carried out in this vein over the course of the MURI. In broad terms, the highlighted cells represent the scope of the research as originally envisioned. A ‘model’ main-chain thermotropic, DHMS-7,9 was selected as a vehicle for fundamental studies allowing development of connections between molecular characteristics (flexibility, molecular weight), fundamental nematic properties & defect dynamics, and the development of macroscopic orientation by shear flow and its connection to rheology. At the opposite extreme, early on within the MURI we initiated studies of commercial thermotropes in complex extrusion-fed channel flow to learn how complex flows during processing influence molecular orientation. The other entries in the table represent efforts to bring these two disparate lines of inquiry, and to extend the scope of our studies to other systems.

Scope of Structural LCP Research							
	Mesogen-Jacketed	DHMS-7,9	PSHQ-6,12	Vectra B	Thermo-tropic HPC	'Bridge' Xydar	Xydar
Synthesis	●	●	Collab.	○		Collab.	
Monodomain Studies		●		‡		○	
Defect Studies		●				○	
Rheology	●	●	Collab.	●		○	
Orientation: Shear		●	●	●	○		
Orientation: Channel Flow		●		●	●	○	●

Filled circles represent definitive experiments. Open circles represent attempted experiments that led to equivocal results. 'Collab' indicates work performed outside the MURI in collaboration with MURI PIs.

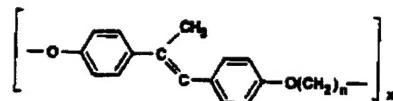
In addition to the central axis of the thrust's research, articulated above and reported upon in greater detail below, thrust members devoted considerable effort in the development and implementation of new concepts in LCP synthetic chemistry and materials science. Mesogen-jacketed LCPs (Ober), new ROMP-based chemistries for LC thermosets (Grubbs & Ober), and the exploitation of specific aryl-perfluoroaryl interactions to stabilize discotic LCs (Grubbs) are among the innovative topics that were pursued in this thrust. There have also been notable cross-over projects between this thrust and other activities in the MURI. Indeed, applications of polymers have permeated in several ways in the other MURI thrusts. In the most noteworthy example, the original leader of the LCP thrust (Thomas from MIT) became progressively more involved in electro-optic thrust of the MURI after it became evident how his research on LCP diblock copolymers has provided the foundation for new approaches to using self-assembled polymers for photonic band gap materials for electro-optic applications. Other examples include use of high molecular weight SGLCPs dissolved in nematic solvents as a test bed for evaluating polymer gels as stabilizers for LC displays (Kornfield), studies of the electro-optic-mechanical response of nematic and cholesteric gels in the electro-optics thrust (Palfy-Muhoray), and studies of polymers for 3-D two-photon microfabrication within the laser-hardening thrust (Ober/Perry/Marder).

## B. Overview of Expertise and Contributions of MURI Team Members & Partners

Pursuit of the ambitious goals of this thrust group required integration of diverse expertise within the overall framework described above. This section briefly highlights the way in which the MURI PIs and industrial & academic partners brought many skills to these problems over the course of the MURI, organized in terms of the experimental hierarchy introduced above.

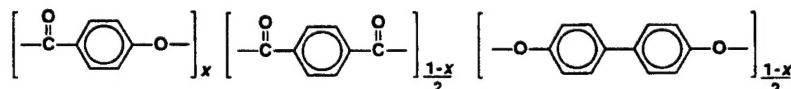
## 1. Synthesis and Scale-up

### (a) DHMS-7,9: The workhorse polymer.



DHMS-7,9 was identified early in the MURI as the central 'model' thermotropic LCP around which experiments would be organized. It is a 'segmented' main-chain LCP, with mesogenic units alternating with flexible spacers of length 7 & 9 units in a random copolymer. Expertise for synthesis of DHMS-7,9 originated with **Ober** at Cornell, and was transferred to **Kornfield** at Caltech. To facilitate the range of experiments envisioned within our program, it was necessary to scale the synthesis of this polymer up to ~100 g scales, something accomplished in Kornfield's group taking advantage of synthesis facilities in **Grubbs'** lab. The scale-up was also facilitated by a donation of DHMS monomer by **Bob Bubeck** and **Dow**.

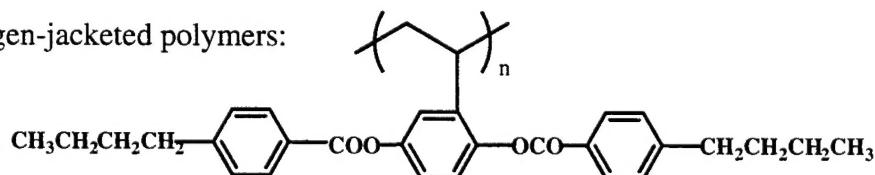
### (b) Xydar®: Commercial & 'Bridge' Materials



Xydar® is typical of commercial fully aromatic copolymers. The lack of any aliphatic spacers in the backbone means that these molecules are quite stiff. If homopolymers were made from similar monomers, their melting points would be unattainably high. Random copolymerization inhibits formation of highly perfect crystallites, suppressing the melting temperature to attainable values. Still, typical commercial LCPs melt at high temperatures, around 300 to 350°C. This can be extremely valuable for their commercial applications, but renders fundamental studies rather difficult. Since most commercial LCPs are sold with fillers, it is also difficult to find the unfilled polymer needed to focus on issues of flow-molecular orientation relationships. In our thrust, we partnered with **Amoco** to provide materials for our studies. **Barry Dean** originally provided substantial quantities of unfilled commercial grade Xydar® resins, while **Jan Nel** subsequently provided specially modified materials with high end cap density (to suppress molecular weight and viscosity) and small amounts of hydrocarbon spacer (in an attempt to move slightly towards the architecture of DHMS-7,9).

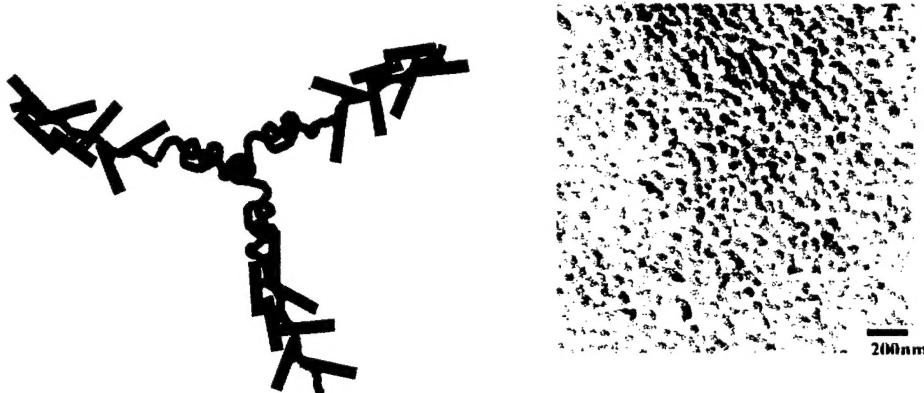
### (c) Other synthetic activities

#### (i) Mesogen-jacketed polymers:

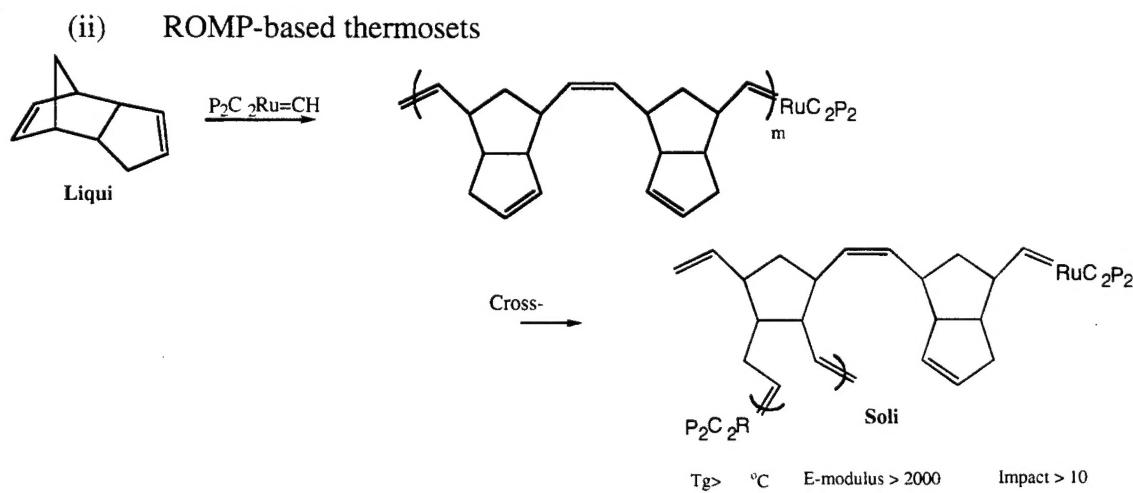


**Ober** developed a novel LCP architecture in which side-chains are tightly coupled to a conventional vinyl polymer backbone. Unlike ordinary side-chain LCPs, in which the mesogen itself is the active element in promoting liquid crystallinity, it is hypothesized that the highly

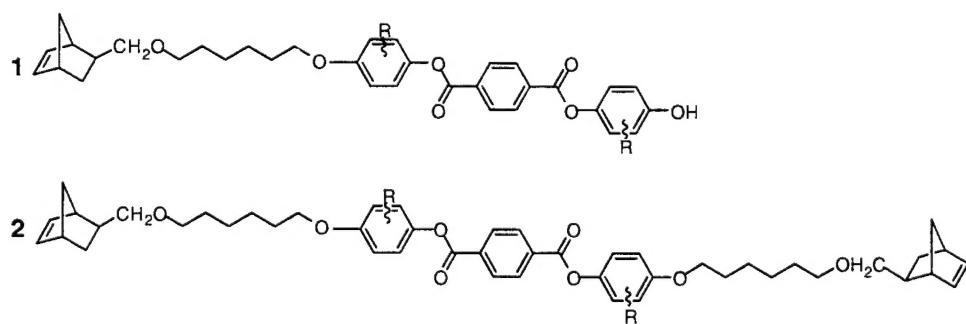
constrained nature of these highly substituted polymers leads to extended chain conformations, which lead to liquid crystallinity. The polymerization is carried out using living free radical methods, which leads to excellent control over molecular weight distribution, and allows for more novel chain architectures through copolymerizations and multifunctional initiation (Figure 1).



**Figure 1.** Schematic of 3-armed star mesogen-jacketed LC-polystyrene block copolymer, along with TEM image of microphase separated morphology exhibited by this polymer.

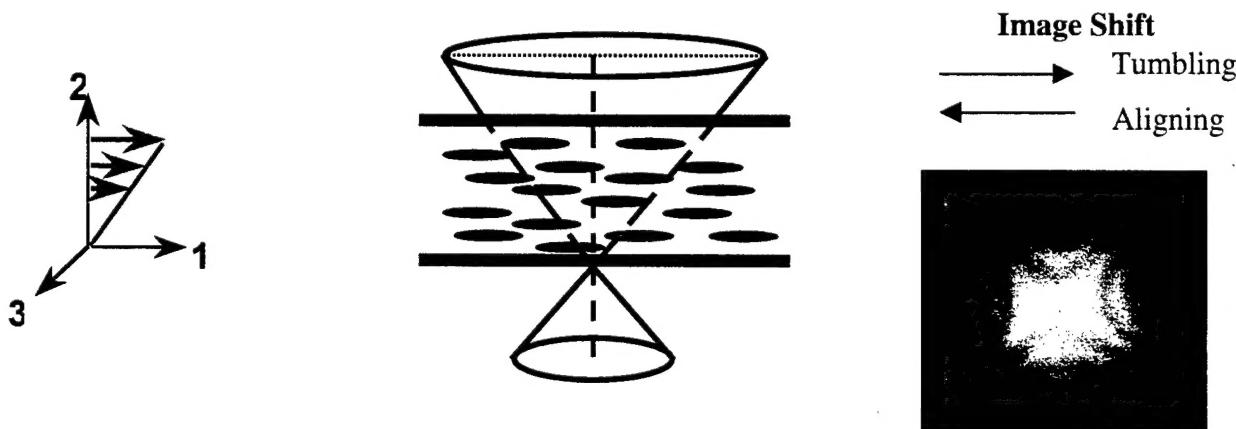


During the MURI kick-off meeting, **Grubbs** realized that a ROMP-based thermoset developed in his group (PolyDCPD) had significant potential as a binder for solid rocket binder, a direction which led to immediate impact on airforce needs. Later, Grubbs and Ober collaborated on the development of ROMP-based chemistry for the polymerization of LC thermoset materials:



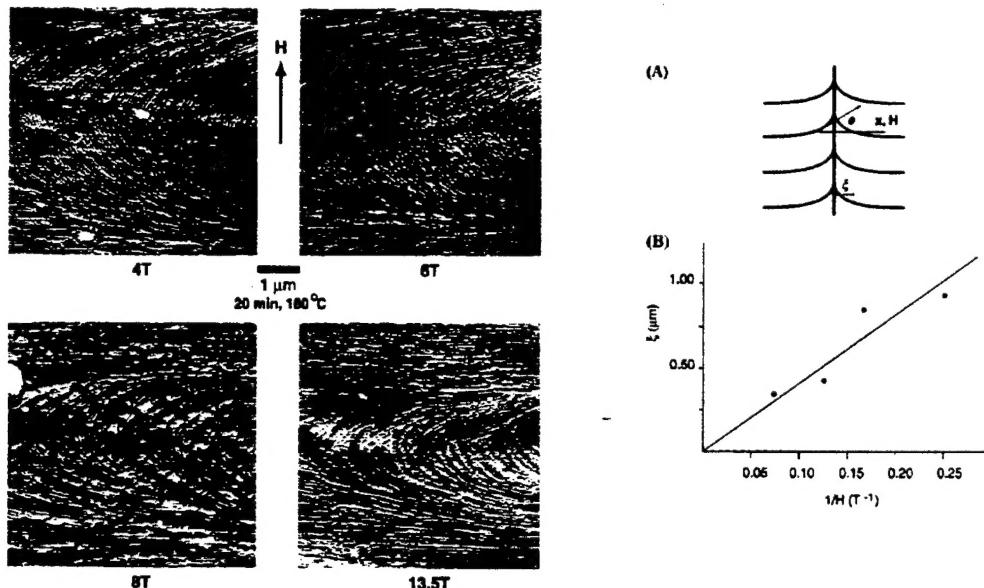
## 2. Fundamental Molecular and LC Characteristics

**Kornfield's** group performed detailed characterization of the effect of molecular weight on the rheology of DHMS-7,9, performing (i) rotational viscosity measurements by studying director re-orientation in a magnetic field, (ii) steady state viscosity measurements, and (iii) viscosity of oscillatory-shear-aligned samples. The onset MW for significant chain flexibility effects (owing to the hydrocarbon spacers) could be determined by a change in behavior. **Kornfield's** group also performed an extremely demanding conoscopic determination of the nematic 'tumbling parameter',  $\lambda$ , in DHMS-7,9. Determination of  $\lambda$  is perhaps the single most important step in unraveling how flow fields influence molecular orientation in LCs. (When  $|\lambda| > 1$ , shear flow promotes uniform orientation at a 'flow-alignment' angle, while when  $|\lambda| < 1$ , shear promotes continuous rotation of the director, or 'tumbling'.) At the start of the MURI, lyotropic LCPs (solutions of rodlike polymers) were known to be tumbling, but very little was known about main-chain thermotropes. In particular, there were no direct quantitative measurements of  $\lambda$  in any main-chain thermotropic polymer. **Kornfield's** group measured this quantity directly using an optical conoscopy technique (Figure 2). The major difficulty is obtaining defect-free monodomain samples, something routinely possible in low-MW nematics, but very difficult in LCPs owing to their high viscosity and high defect density.



**Figure 2.** Principle of monodomain conoscopy experiment. A planar LCP monodomain generates a hyperbolic fringe pattern when viewed with conoscopic illumination. Upon inception of shear flow, the material may be classified as tumbling or aligning depending on whether the image shifts in the flow direction or opposite the flow direction. Analysis of the displacement as a function of applied strain allows quantitative determination of  $\lambda$ .

At MIT, **Thomas** performed microscopic studies of defect annihilation in both DHMS-7,9 and low molecular weight Xydar samples. **Thomas** also performed detailed analysis of director profiles in the vicinity of inversion walls under the influence of an applied magnetic field (Figure 3). Analysis of how the curvature in the director field changes with applied field strength provides a measure of elastic constant anisotropy.



**Figure 3.** TEM visualization of main-chain LCP director fields in vicinity of an inversion wall under applied field. Analysis of these patterns leads to elastic anisotropy  $K_{11}/K_{33} \approx 3$ .

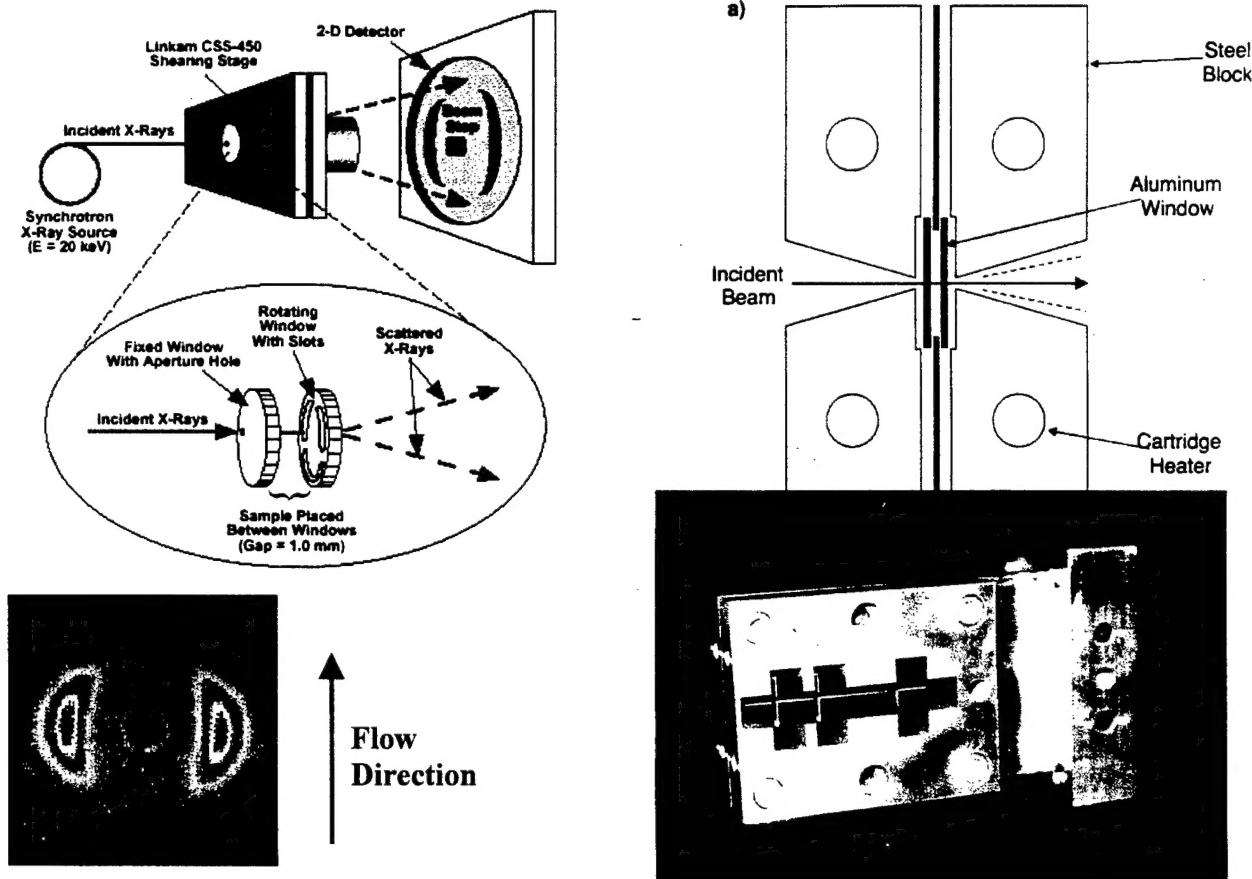
MURI investigators also collaborated with others to further pursue detailed molecular and nematic characterization studies. **Burghardt** collaborated with **Mark Dadmun** (University of Tennessee) on SANS measurements of deuterium-labeled DHMS-7,9 to look at the anisotropy in the coil shape in magnetically aligned samples. **Burghardt** also collaborated with **Claudia Schmidt** (University of Freiburg) on the application of rheo-NMR methods capable of determining various Leslie constants of LCPs to a DHMS-7,9 sample.

### 3. Orientation development, texture & rheology in shear flow

These studies were part of a close collaboration between **Kornfield** and **Burghardt**. **Kornfield**'s group performed detailed steady state and transient rheological characterization of DHMS-7,9, Vectra® and Xydar® polymers, as well as direct microscopic visualization of the evolution of the polydomain structure during shear using *in situ* polarizing optical microscopy. **Burghardt**'s primary focus was on *in situ* x-ray scattering studies of macroscopic molecular orientation, taking advantage of synchrotron research facilities at the **DuPont-Northwestern-Dow** team at the Advanced Photon Source. These studies employed a rotating parallel disk shear cell that allows direct x-ray access during shear (Figure 4).

### 4. Towards processing: Orientation development in complex flows

Studies of molecular orientation development in complex channel flows were pursued mainly by **Burghardt**, in frequent collaboration with **Kornfield**, again using *in situ* x-ray scattering. An x-ray capable extrusion die was conducted to allow direct probing of fluid structure as a function of position in slit-channel flows with expansions or contractions in cross-sectional area, or flow past obstructions & bends (Figure 4).



**Figure 4.** Experimental capabilities for in situ x-rays scattering measurements of molecular orientation in thermotropic LCPs. The left diagram shows a schematic of the rotating disk shear cell used for measurements in simple shear flow along with a representative 2-D x-ray scattering image, while the right diagram shows a cross-sectional view of the channel flow die used to study molecular orientation in complex flows, along with a photograph of the assembled die.

### C. Accomplishments and New Findings

#### 1. Summary

Here we briefly summarize the major scientific contributions from our MURI-sponsored research on main-chain liquid crystalline polymers. A slightly expanded discussion of each topic, along with representative results, follows below.

- (a) We performed the first ever quantitative measurements of the tumbling parameter,  $\lambda$ , in a main-chain thermotropic polymer. It was determined that DHMS-7,9 is flow aligning, a fact which is attributed to the effects of chain flexibility manifested in other characterization experiments, and as predicted by molecular theories. This contrasts strongly with behavior in lyotropic LCPs, and renders

much of the existing body of knowledge on lyotropes useless in predicting or interpreting the behavior of semi-flexible thermotropes.

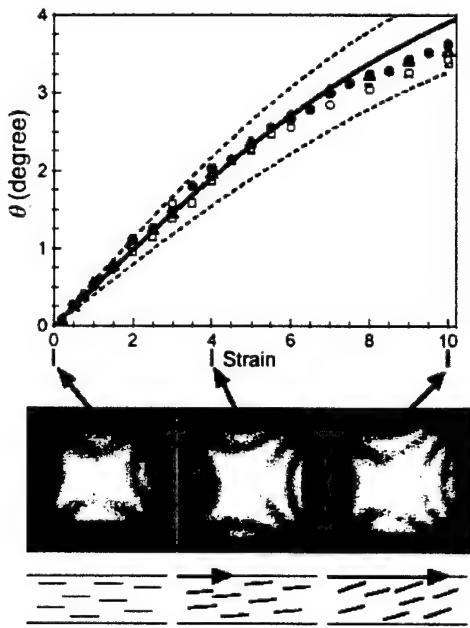
- (b) We have performed comprehensive and coordinated measurements of texture, rheology and molecular orientation in steady and transient shear flows of DHMS-7,9. This is the first time that structural and mechanical data were collected in such close coordination and in such a wide range of conditions. In addition, knowledge of the flow-aligning character of DHMS-7,9 allows detailed interpretation and modeling of the rheology and orientation development than is possible with any other material.
- (c) We have assembled a comprehensive database on how complex flow kinematics with mixed shear and extension affect molecular orientation of commercial thermotropes. Here, too, we have explored the ability to model the orientation response, although current models are unable to predict behavior in detail. Perhaps most importantly, we have learned that, paradoxically, behavior in very complex flows might provide an indirect way to probe the tumbling/aligning characteristics of commercial materials for which application of direct methods (such as monodomain conoscopy) is not possible.
- (d) Combining these results leads to an emerging picture for the role of chain flexibility. Direct evidence shows that main-chain thermotropes with high flexibility (e.g. DHMS-7,9) exhibit flow aligning behavior, while indirect evidence from complex flows and rheology suggests that commercial thermotropes, which are more stiff at the molecular level, exhibit director tumbling. Such insights are invaluable in trying to rationally anticipate the orientation behavior of commercial LCPs under realistic processing conditions, and suggest possible routes to modify chain architecture to influence the evolution of molecular orientation under flow.

## 2. *Representative Results*

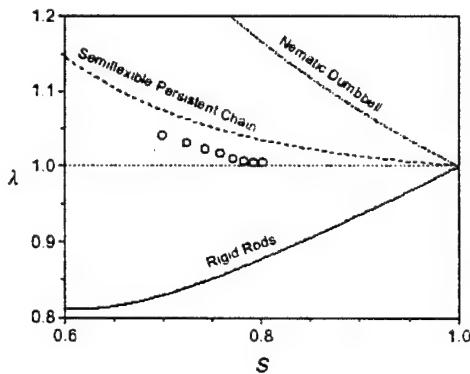
### (a) Monodomain conoscopy

Figures 5 and 6 illustrate application of the monodomain conoscopy technique to a monodomain of DHMS-7,9 with molecular weight of approximately 11,000. This low molecular weight is required to lower the viscosity. Even so, formation of a monodomain typically requires 24 – 48 hours of annealing in a 7T superconducting magnet. Only the high thermal stability and moderate operating temperature of the model DHMS-7,9 polymer make such an experiment possible. Following the procedure in Figure 2 above, a planar monodomain is subjected to inception of shear flow at a very low rate. The images were seen to shift against the flow direction, unambiguously identifying DHMS-7,9 as flow aligning. The conoscopic images were analyzed to determine how much the director rotates as a function of strain (Figure 5); these quantitative data allow determination of  $\lambda$  to a high degree of precision ( $= 1.05$  in this example). Repeating the experiment at a range of temperatures throughout the nematic phase allows quantitative testing of various theories for rigid and semiflexible polymers (Figure 6; here

birefringence data were independently analyzed to determine the molecular order parameter at each undercooling). Note that over the entire nematic range, the value of  $\lambda$  is extremely close to, but always greater than, unity. These data suggest that the semi-flexible wormlike chain model of Semenov comes closest to describing the behavior observed in DHMS-7,9. The negative deviations from the theory may reflect the fact that, at this low molecular weight, the effects of flexibility are not yet fully developed.



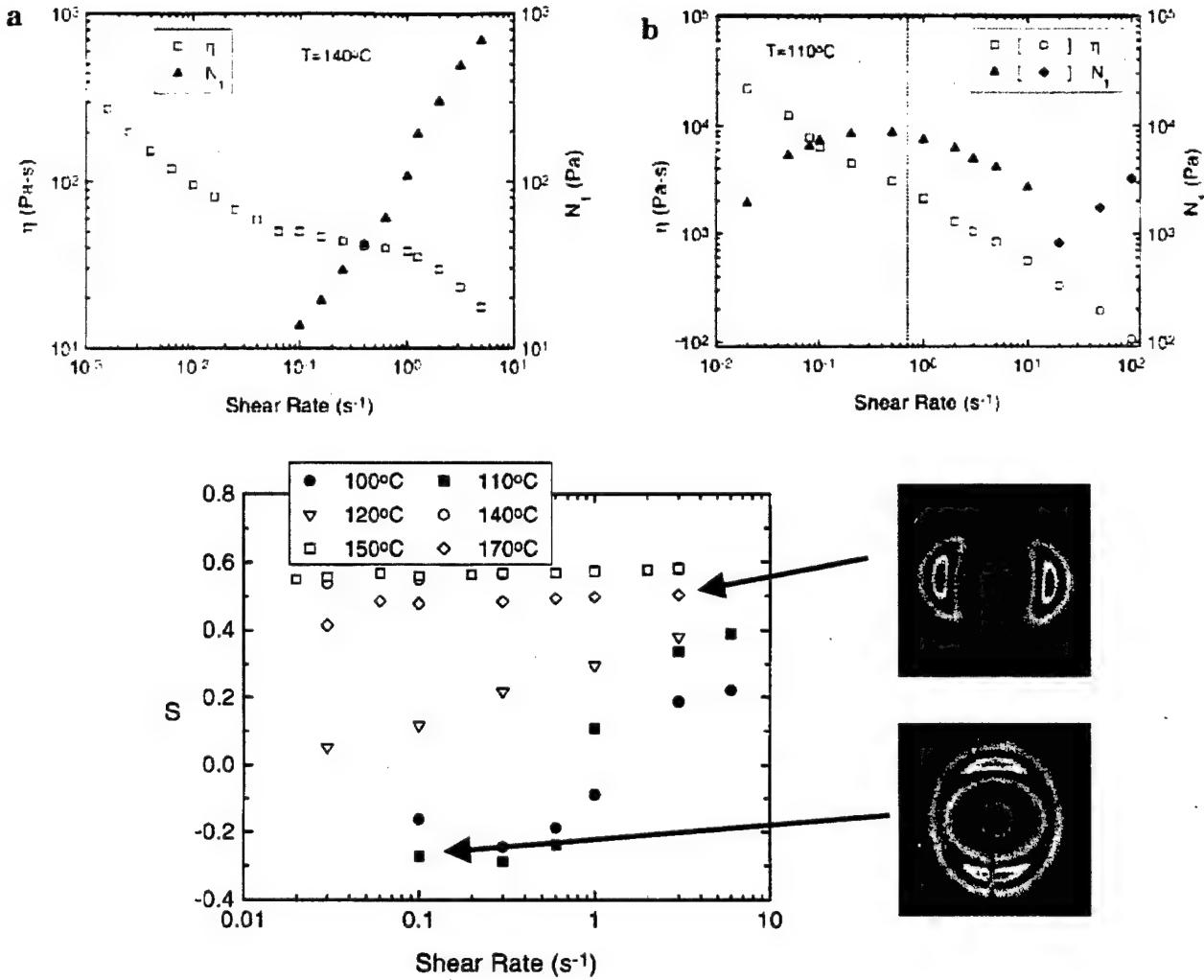
**Figure 5.** Director rotation as a function of applied strain in DHMS-7,9 monodomain at  $T = 130^\circ\text{C}$ . Analysis using Leslie-Ericksen theory gives  $\lambda = 1.05$ .



**Figure 6.** Tumbling parameter as a function of molecular order parameter, compared against predictions of molecular theory.

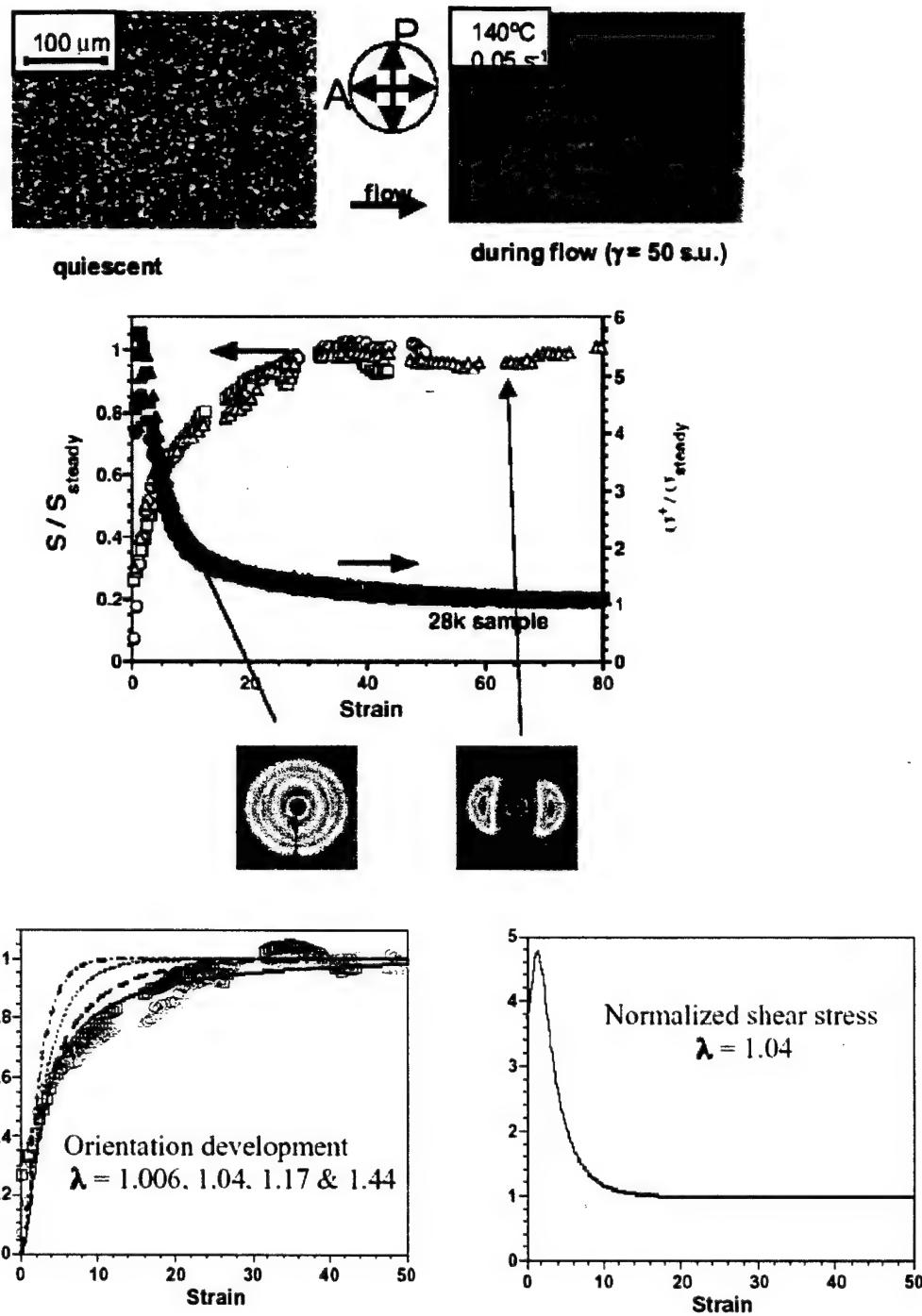
(b) Texture, orientation and rheology in shear flow.

Within the nematic phase, DHMS-7,9 exhibits a classic ‘3-region’ flow curve, in which an additional regime of shear thinning is found to be present at low shear rates (Figure 7a). Below temperatures of around  $120^\circ\text{C}$ , there is a transition to a more highly structured phase (‘phase-x’), resulting in a two order-of-magnitude increase in the viscosity (Figure 7b). X-ray diffraction experiments performed by Clark’s group suggest that there is a weakly organized layer-like structure in DHMS-7,9 under these conditions. In situ x-ray measurements show that phase-x has a profound affect on the molecular orientation under flow. In the nematic phase, there is essentially a featureless constant degree of orientation along the flow direction (in agreement with expectations for a shear aligning nematic). On the other hand, within phase-x at low rates the orientation flips so that mesogens are oriented perpendicular to the flow direction. Shearing at higher rates is able to flip the mesogens back towards the flow direction, presumably as a result of disrupting the poorly defined layered structure present within phase-x.



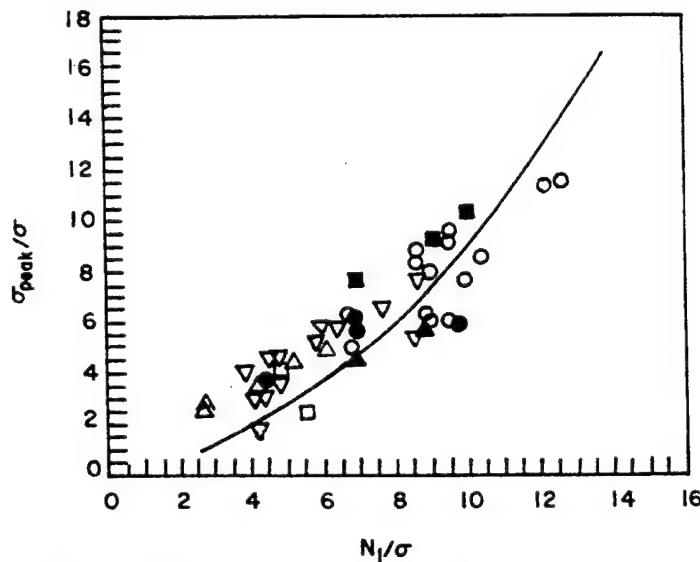
**Figure 7.** Steady state rheology and structure of DHMS-7,9 (28k MW). (a) Viscosity and  $N_1$  as a function of shear rate in nematic phase (140°C). (b) Viscosity and  $N_1$  as a function of shear rate in phase-x (110°C). (c) Molecular orientation as a function of shear rate for a range of temperatures.

Transient rheological and structural experiments provide more revealing insights into the nature of orientation development and its connection to rheology in DHMS-7,9. Here we consider only inception from a random polydomain (i.e. the state that results from quenching from the isotropic to the nematic phase). Figure 8 illustrates behavior observed upon flow inception from a random polydomain. The initially grainy polydomain structure becomes more uniform as the sample is sheared. Measurements of molecular orientation exhibit a monotonic growth to their steady state value, while shear stress exhibits a single, large overshoot. The orientation behavior is consistent with expectations for shear alignment, and contrasts with the oscillatory response typically observed in tumbling lyotropic LCPs.



**Figure 8.** Flow inception behavior of DHMS-7,9 (28k MW). Top panel shows polarized optical micrographs of initial polydomain texture and the smooth texture observed following prolonged shearing. Middle panel compares x-ray measurements of molecular orientation with transient mechanical shear stress data. Note that all transient data scale very well with applied strain. Bottom panels show predictions of polydomain Ericksen model predictions of orientation development and transient shear stress.

We have explored a very simple modeling approach in an attempt to rationalize the behavior of orientation and shear stress upon flow inception from a random initial condition. We postulate that the orientation in each ‘domain’ evolves according to Ericksen’s transversely isotropic fluid model, independent of its neighbors (that is, we ignore all effects of distortional elasticity). An ensemble of random initial conditions is generated, and then each domain is simulated forward in time. Suitable ensemble averages allow extraction of the development of orientation and shear stress. The results are found to agree very well with the data (Figure 8). Using this approach, the only required material parameter is the tumbling parameter,  $\lambda$ . Note that the development of orientation may be very well described by using values of  $\lambda$  very near, but greater than 1. This agrees well with the conoscopic determination of 1 in DHMS-7,9 described earlier (Figure 6). Similar values of  $\lambda$  are also found to represent the qualitative transient shear stress behavior, and particularly the magnitude of the shear stress overshoot, very well. From these polydomain simulations we have learned that the polydomain model, together with existing molecular models of shear aligning nematic polymers, predicts a universal correlation between the magnitude of shear stress overshoots observed upon inception from a random polydomain initial condition and the *steady state* ratio of normal stress to shear stress. In collaboration with **C. D. Han** of the University of Akron, we have tested this prediction against a wide range of data collected by Han on another family of semi-flexible ‘segmented’ main-chain LCPs (PxHQn); as seen in Figure 9, the prediction holds up extremely well to this stringent test. Such results illustrate the power of the comprehensive approach taken within the MURI. The existence of large shear stress overshoots in thermotropic LCPs has been well known for decades, but owing to our detailed understanding of the dynamics in the DHMS-7,9 system, we are afforded the opportunity to adopt a more quantitative stance towards the data, and develop new understanding about the structural origins of previously poorly understood rheological phenomena.



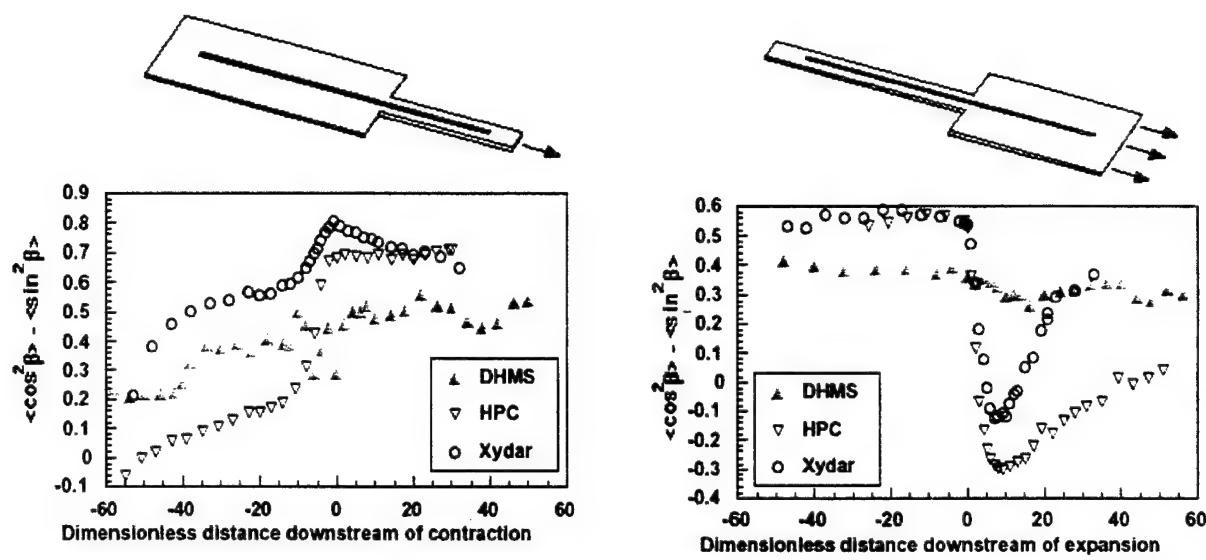
**Figure 9.** Parameter-free test of polydomain model predictions of shear stress overshoots in shear-aligning thermotropic LCPs upon flow inception, using mechanical inception data from the group of C. D. Han.

(c) Orientation in complex flows.

Extensional flows are well-known to promote high degrees of molecular orientation in both flexible and rigid polymers alike. In the case of LCPs, shear flow may or may not promote high degrees of molecular orientation depending on whether the nematic is shear aligning or tumbling. Flows which combine both shear and extension are thus interesting in that there can be competition between the orienting effects of extension against the disorienting effects of shear. If the extension axis is orthogonal to the flow direction, the converse situation can arise, in which shear promotes orientation along the flow direction while extension promotes orientation perpendicular to the flow direction. In addition to academic interest, these mixed flows are precisely the types of kinematics encountered in processing operations such as extrusion and injection molding. Hence, understanding the factors which affect molecular orientation can favorably impact processing strategies.

Using the x-ray channel flow die, we have pursued extensive *in situ* measurements of molecular orientation in three thermotropic LCPs (Xydar®, Vectra B® and thermotropic hydroxypropylcellulose). In addition to the direct value of such data, this type of experiment also has the potential to be informative about the underlying dynamic classification of the polymer. This can be understood by noting that if a material is shear aligning, then shear flow upstream of a contraction will already be effective in promoting a high degree of molecular orientation. Hence, there is little potential for added extension to further increase molecular orientation. Conversely, director tumbling leads to a degraded amount of orientation in shear-dominated regions, and hence superimposed extension can significantly (albeit temporarily) enhance the overall degree of orientation. These heuristic arguments were further explored using polydomain model simulation similar to those described above, and found to be robust: tumbling materials are, in general, more susceptible to the effects of superimposed extension than shear-aligning materials.

The potential benefit of this viewpoint is evident in Figure 10. Here we plot measurements of molecular orientation along the centerline in 4:1 slit-contraction and 1:4 slit-expansion flows, for Xydar®, thermotropic HPC and DHMS-7,9. While the Xydar and HPC data were collected *in situ* using the channel flow die, the DHMS-7,9 data were collected on a quenched solid specimen that had been subjected to a geometrically similar flow field. As discussed above, DHMS-7,9 is known to be shear aligning. Consistent with this, there is no significant change in the degree of molecular orientation along the flow direction in the vicinity of a contraction, and only a weak loss of orientation following an expansion. In contrast, both other materials exhibit a very pronounced increase in orientation at the contraction. In the case of Xydar, this is followed by a distinct loss of orientation downstream of the contraction, which should be a strong (if indirect) indicator that Xydar® is of the tumbling type. Similar data have been collected more recently using Vectra B, for which no definitive data exist, but where certain transient data indicate director tumbling. Such temporary increases in molecular orientation have also been documented in slit flows of lyotropic LCPs for which tumbling is known to occur. These results appear to constitute the best available evidence that common commercial thermotropic LCPs are of the tumbling type. This fits with the overall picture that shear aligning dynamics in DHMS-7,9 result from chain flexibility, since commercial LCPs have much less backbone-level flexibility.



**Figure 10.** Comparison of centerline axial distributions of molecular orientation in slit-contraction (left) and slit-expansion (right) flows of main chain thermotropes Xydar, HPC and DHMS-7,9.

## II. Display and Beam Steering Thrust

Noel Clark, University of Colorado

Larry Dalton, University of Southern California

Julie Kornfield, California Institute of Technology

Seth Marder, University of Arizona

Christopher Ober, Cornell University

Peter Palffy-Muhoray, Kent State University

Joe Perry, University of Arizona

Ned Thomas, Massachusetts Institute of Technology

David Walba, University of Colorado

### A. Overview of Thrust

The objectives of the Display and Beam Steering Thrust of the AFOSR Liquid Crystal MURI are to address key materials and device technology issues affecting performance of liquid crystal (LC) electro-optic (EO) devices. Of particular interest are device structures useful in information *Displays* and for *Laser Beam Steering and Switching*. Two basic themes are development of bulk LCs having high performance characteristics (nematic LCs, and chiral smectic LC devices having analog response), and development of novel LC electro-optic structures. Research on novel device structures focuses on *LC Alignment* and on *photonic band-gap* materials.

**Technical highlights from the MURI effort are:**

#### 1. *V-shaped Switching in Tilted Chiral Smectic Liquid Crystals*

Thresholdless switching has been observed in specially developed chiral smectic liquid crystals. Display cells utilizing these materials show a nearly linear dependence of transmittance on applied voltage. Space charge effects screen the electric field in the liquid crystal, and “stiffening” of the polarization causes the material to orient as a uniform whole. The detailed understanding of this underlying mechanism which has been gained under this MURI opens the door to the construction of a new generation of grayscale active matrix liquid crystal displays with high contrast and vastly improved response times.

#### 2. *Mirrorless Lasing in Cholesteric Liquid Crystalline Materials*

Due to their inherently periodic structure, cholesteric liquid crystals are one-dimensional photonic band-gap materials. In addition to their utility as switchable mirrors for beam steering applications, optically pumped thin cholesteric liquid crystal films, either low molecular weight liquids or liquid crystal polymers, can simultaneously act both as the distributed cavity host and the active medium, and emit laser radiation at the reflection band edge. Such films can enhance the emission spectrum and directionality of backlights for liquid crystal displays, and serve as organic thin film low

threshold tunable laser light sources. Liquid crystalline elastomers are particularly interesting, since the reflection band edge and hence the lasing wavelength can be tuned by stretching the elastomer sample. Cholesteric elastomers can therefore act as tunable laser sources, as well as elements for remote sensing. The blue phases BP I and BP II are defect lattices with periodicity in three dimensions, hence they form self-assembled 3-d photonic band gap structures. Recently observations of lasing in these materials is the first observation of lasing 3-d PBG systems.

### *3. Brownian Ratchet Mechanism in Photobuffing of Liquid Crystal Alignment Layers*

Optically induced anisotropy in photosensitive alignment layers has been shown to effectively align liquid crystals. In addition to overcoming problems associated with conventional mechanical rubbing, photobuffing allows spatially and temporally varying liquid crystal alignment. Understanding the underlying “orientational ratchet” mechanism, where light effectively exerts a torque on the material without the transfer of angular momentum, allows accurate control of the alignment layer anisotropy and subsequent liquid crystal alignment. In addition to use in the manufacture of flat panel displays, photobuffing enables the implementation of liquid crystal technology on curved plastic substrates, such as switchable/tunable filters and polarizers for eye protection, and ambient light control elements for the visors of helmet mounted displays.

### *4. Optomechanical Response of Nematic Liquid Crystal Elastomers*

Liquid crystalline elastomers are mesogen containing rubbers, characterized by coupling between orientational order and mechanical strain. In addition to changing their optical properties when subjected to mechanical deformations, changing the order parameter of these materials results in strain and a change of macroscopic conformation. A particularly efficient method of changing the order parameter is by light. Illuminating dye containing liquid crystal elastomers can dramatically change the order parameter, and result in large and rapid changes in shape of the sample. The coupling allows a new way of changing the orientational order, resulting in a new mechanism for the optomechanical response, making these materials ideal candidates for a variety of applications as optomechanical actuators, artificial muscles and adaptive optical elements.

## **B. Status of Electro-Optics Efforts in PI Laboratories**

### *University of Arizona*

Much of the work of the Arizona group is discussed in the Laser Hardening Thrust. **Marder** and **Wu** have collaborated to develop a series of colorless, high dielectric anisotropy dopants for use in lowering the operational voltage of LC compositions. These new dopants are significant in a wide range of electro-optic devices spanning displays, beam steering and laser hardening. A joint Caltech/Hughes patent has been filed on these materials.

Two-photon dyes have been synthesized by **Marder**; characterization of these is currently under way by **Perry** and **Palffy-Muhoray**. These materials may be useful for high resolution photoalignment, as well as in the construction of photonic band-gap structures.

**Marder** and **Perry** have synthesized a new class of disk-like mesogens for electron transport applications. Work on characterizing a series of these compounds has recently been started in collaboration with the groups of **Palffy-Muhoray**, **Clark** and **Kornfield**.

**Perry**, **Marder**, and **Ober** are also exploring the use of positive-tone 3D microlithography for fabricating switchable microoptical devices.

#### *California Institute of Technology*

Toward the goal of preparing highly dilute liquid crystalline gels, we have developed synthetic methods that can successfully produce very high molecular weight ( $\sim 1 \times 10^6$  g/mol) side group liquid crystalline polymers (SGLCPs). **Kornfield**'s work on LC gels is highly collaborative, with input from the **Ober** group in optimizing the synthesis, from Shin-Tson **Wu** at Hughes in electro-optic measurements on nematics and from Noel **Clark** and Dave **Walba** on molecular design of FLC gels and their characterization. Conoscopic methods have been employed to observe the effect of low concentrations (<10%) of ultra-long SG-LCP on the orientational response of a low molar mass LC host. Unprecedented transformations of alignment character were induced, as described below. Triblock polymers with very long SGLCP midblocks flanked by endblocks that separate from the LC to form physical crosslinks have been demonstrated to self-assemble reversible gels in nematic solvents, producing materials with exceptional optical uniformity relative to prior routes to LC gels.

#### *University of Colorado*

**Clark** and **Walba**'s emphasis this year has focused on synthetic and physical studies of analog electro-optic effects in ferroelectric liquid crystals, and on a novel liquid crystalline material for optical fibers for non-linear optical applications. The former is directed at the design of a new generation of analog chiral smectic displays, while the aim of the latter is toward ferroelectric liquid crystal nonlinear optic fibers with a photonic bandgap. In addition to studying and characterizing alignment layers produced by **Palffy-Muhoray**, a new effort has started in carrying out photobuffing at Colorado to enable the realization of bookshelf textures using photoalignment techniques.

#### *Cornell University*

Block copolymers are gaining more and more attention both for fundamental research and for industrial applications due to their nanoscale microstructures and the capability of combining many desired properties into a single molecule. **Ober** is investigating side-group modified liquid crystalline block copolymers (SGLCBCP) not only because of their specific microphase structures but also the advanced applications made possible by liquid crystallinity, for example, microphase stabilized ferroelectric liquid crystals. Though the covalently bonded SGLCBCPs possess interesting properties, there are still limitations due to their complex synthesis and the slow response. Instead, hydrogen bonding may offer an easier way to modify composition and the possibility of increasing the switching response speed since the hydrogen bonds are strong enough to form stable links between the polymer backbone and the side groups, but not so strong as to hinder mobility of

the side groups. This approach provides a route to fine-tune the volume ratio between the two blocks by addition of the desired amounts of side groups and to tune the properties (e.g. refractive index) of the LC block by adding the additional moieties. The combination of a periodic nanostructure and liquid crystallinity offers us an exciting approach to make photonic band gap (PBG) materials which could be very useful in the communication industry.

#### *Kent State University*

The main efforts of **Palffy-Muhoray**'s group during the MURI have been directed at understanding:

1. the dynamics of photoinduced reorientation and photobuffing
2. mirrorless lasing in cholesteric liquid crystalline materials, and
3. the study of the optomechanical response of liquid crystalline elastomers.

Both experimental and theoretical work has been carried out to probe the mechanism of light induced reorientation in liquid crystals. This included the measurement of optical nonlinearities in dyed liquid crystals, and the measurement photoinduced anisotropy in photosensitive alignment layers. The results were interpreted in terms of a generalized Fokker-Planck model.

Cholesteric liquid crystals are self-assembled photonic band-gap materials. The band structure gives rise to distributed cavity effects which allow population inversion in optically pumped samples, and mirrorless lasing. Fluorescent emission and lasing have been studied in low molecular weight liquid crystals, and in free standing liquid crystalline polymers and elastomers.

Recently, the optomechanical response of liquid crystalline elastomers has been studied. The dynamic response of azo-dye doped nematic elastomers has been characterized as function of irradiation intensity, wavelength, and dye concentration.

#### *Massachusetts Institute of Technology*

The main objective of **Thomas**'s recent efforts was to fabricate a self-assembled tunable optical switch in the visible using block copolymers with side chain liquid crystalline blocks in collaboration with **Ober**. This task built upon the knowledge gained in the early years of the MURI in learning how to control the morphology of liquid crystalline polymers and on an understanding of simple 1D periodic optical systems. Hydrogen bonding was used to deliberately induce the formation of a liquid crystalline mesophase in one block of a suitable coil-coil diblock copolymer host. The incorporation of liquid crystallinity in a block copolymer results in an active material: a temperature dependent, limited photonic band gap in the visible has been demonstrated. A poly(styrene-*b*-methacrylic acid), P(S-*b*-MAA), block copolymer was anionically synthesized and then imidazole terminated mesogens were selectively sequestered into the methacrylic acid block via hydrogen bonding with the hydroxy group, simultaneously augmenting the molecular weight and adding mesogenic function to the block copolymer. The P(S-*b*-MAA/LC) self assembles by simple solvent casting into a 1D lamellar microdomain structure with a 175 nm period. The as-formed structure exhibits an optical stop band in the green. The center of the stop band can be reversibly red shifted by approximately 10 nm using a temperature change of 50 °C due to thermally inducing changes in the order parameter of the mesogens in the LC layers. Simulations identify relevant

criteria (refractive indices, mesogen orientation, anchoring conditions and microdomain geometry) that are useful in the design of LC-BCP material systems to achieve particular optical properties.

#### *University of Southern California*

Our research has been focused on three tasks:

1. preparation of new polar tolane liquid crystals for evaluation by Dr. Shin-Tson Wu of HRL Laboratories,
2. development of new theory to better understand order achieved in LC materials characterized by intermolecular electronic electrostatic interactions as well as by shape effects, and
3. attempts to achieve higher order in phase-separation LC systems by exploitation of hydrogen bonding.

### C. Accomplishments and New Findings

#### C.1 Dopants and NLO Dyes: University of Arizona

**Marder** and **Wu** have collaborated to develop a series of colorless, high dielectric anisotropy dopants for lowering the operational voltage of LC compositions. These new dopants are significant in a wide range of electro-optic devices spanning displays, beam steering and laser hardening. A joint Caltech/Hughes patent has been filed on these materials.

Two-photon dyes have been synthesized by **Marder**; characterization of these has been performed by **Perry** and **Palffy-Muhoray**. Among other applications, two-photon dyes are of potential interest in photoalignment, since they allow high spatial resolution, two-beam writing, and a sharper writing threshold. A new two-photon azo-dye YZAZ05 has been synthesized with the structure shown (Figure 1).

Preliminary work in the optical characterization and photoalignment properties of films with YZAZ05 has been carried out at Kent State. The emission and excitation spectra are shown in Fig. 2. Photoalignment layers were prepared with this dye, and laser writing has been demonstrated in a nematic cell filled with E7. The photosensitivity of the alignment layer is extremely high, enabling writing with pump powers as low as 2 mW.

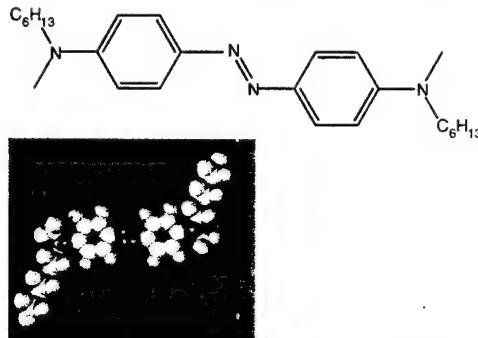


Figure 1. Composition and structure of YZAZ05.

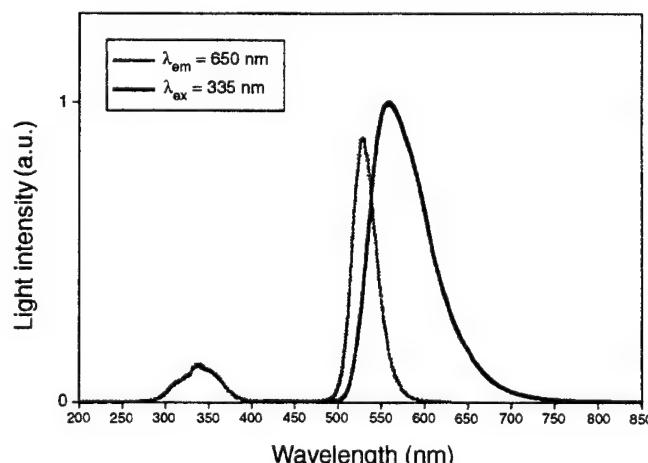


Figure 2. Emission and excitation spectrum of YZAZ05.

**Marder** has synthesized a new class of disk-like mesogens for electron transport applications. Work on characterizing a series of these compounds has recently been started in collaboration with the groups at Kent, Colorado and Caltech.

### C.2 Reversible LC Gels with Exceptional Uniformity: California Institute of Technology

LC elastomers are of interest for diverse applications from actuators and sensors to responsive optical elements. Systematic control of the coupling between the mechanical and optical responses of the materials is needed to improve attributes from the sharpness of their mechanical response to stimuli (temperature, light or electric fields) to the uniformity of their optical properties. Therefore, the MURI team has developed synthetic methods to prepare polymers that self-assemble gels in LC solvents. Because the polymer molecules may be dissolved and characterized, the length of the strands between crosslinks in the physical gel is well defined. By pushing out the limit in the length of side-group liquid crystal polymers that can be prepared by polymer analogous synthesis, this research opens the way to highly uniform liquid crystalline gels with lower polymer concentrations (hence faster electro-optic response) than have been accessible previously. The efforts in the **Kornfield** group are highly collaborative, with input from the **Ober** group in optimizing the synthesis, from Shin-Tson **Wu** at Hughes in electro-optic measurements and from Noel **Clark** and Dave **Walba** on molecular design of FLC gels and their characterization.

Our initial physical studies have examined nematic solutions and gels. **Kornfield** and **Ober** extended polymer analogous synthesis to produce very high molecular weight ( $\sim 1 \times 10^6$  g/mol) side group liquid crystalline polymers (SGLCPs). Solutions of SG-LCP homopolymers have been used to establish the concentration dependence of key liquid crystal properties for electro-optic applications (order parameter, elastic and viscous constants, phases and transition temperatures). Rheo-conoscopy has been employed to observe the effect of low concentrations (<10%) of ultra-long SG-LCP on the orientational response of a low molar mass LC host. Unprecedented transformations of shear alignment character were induced. We have demonstrated adding ultralong, oblate SGLCP to a nematic host can induce not only the familiar change from flow aligning to tumbling, but can

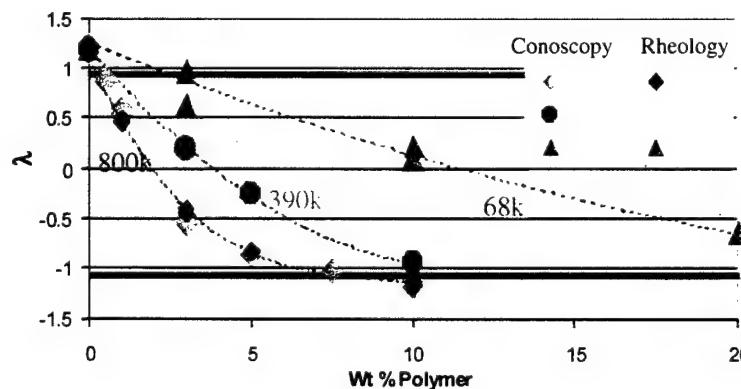


Figure 3. Ultra-long SGLCP shows exceptionally strong effects on the orientational response of the host LC (PBCB6 dissolved in 5CB at 25°C). The observation of a tumbling parameter more negative than -1 is unprecedented; it indicates that the mild orientation of low-concentrations of the 800k g/mol PBCB6 effectively commands the orientation of the director, causing it to align nearly along the velocity gradient direction (perpendicular to the shear alignment direction of all prior flow-aligning calamitic nematics). The effect of SGLCP molecular weight on the effect shows that this behavior is indeed due to the high molecular weight we have been able to reach.

decrease the tumbling parameter so strongly that the material becomes flow aligning again—with the director along the gradient direction! The powerful effect of the polymer on the orientational response of nematics due to flow is demonstrated to be a consequence of the exceptional length of the polymer (Fig. 3).

Based on the observed behavior of these nematic solutions, the orientational behavior of nematic gels was accurately predicted. Advances in the SGLCP synthesis were further used to prepare coil-SGLCP-coil block-polymers designed to self-assemble reversible gels in nematic LC solvents. Ultralong SGLCP triblock copolymers were shown to form highly uniform, self-assembled LC gels. Using very long SGLCP midblocks (~1M g/mol) provided homogenous, single-phase gels with relatively low polymer concentrations (~15% in 5CB of a triblock with 50k PS end blocks and a 1.9M SGLCP midblock with CB side groups). Small applied strain causes the director to align with such uniformity that a conoscopic figure is readily observed (Fig. 4). To our knowledge, no other route to LC gels provides access to this level of optical uniformity. Electro-optic switching is observed, with threshold voltage increased approximately six fold relative to pure 5CB.

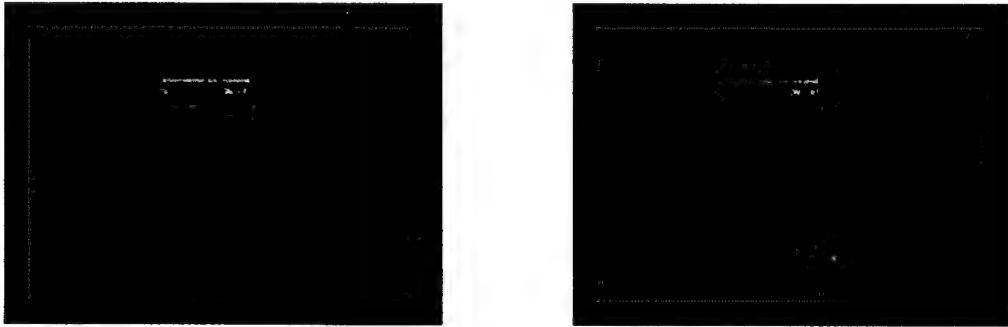


Figure 4. Conoscopic image: left, an unaligned sample of gel; right, the same sample subjected to 100% shear strain. The formation of an interference figure indicates that the director field and order parameter are highly uniform throughout the specimen, a signature of the highly uniform network structure formed by self-assembly. The position of the center of the interference figure indicates that the director is oriented nearly along the gradient direction, as anticipated by the observation of a tumbling parameter more negative than  $-1$  (Figure 3).

In addition to potential applications in roll-to-roll processable LC displays, the nematic gels have potential for “artificial muscles” with sharper thermal transitions than existing LC elastomers. The self-assembly strategy for forming LC gels and using them to align LC phases can now be extended to cholesteric and smectic LCs, including the deVries smectics that exhibit V-shaped switching and the chiral smectic banana phases, neither of which can be aligned by any current method.

**C.3 Analog FLCs and Smectic Polymers for NLO Fiber Optics:** University of Colorado Emphasis at Colorado has focused on synthetic (**Walba**) and physical (**Clark**) studies of analog electro-optic effects in ferroelectric liquid crystals, and on a novel liquid crystalline material for optical fibers for non-linear optical applications. The former is directed at the design of a new generation of analog chiral smectic displays, while the aim of the latter is toward ferroelectric liquid crystal nonlinear optic fibers with a photonic bandgap. In addition to studying and characterizing

alignment layers produced by **Palffy-Muhoray**, a new effort has started in carrying out photobuffing at Colorado to enable the realization of bookshelf textures using photoalignment techniques.<sup>[1]</sup>

Due to the MURI, emphasis on analog EO modulation for optical beam steering and displays, one a key project in the Boulder MURI labs has been studies on the origins of the very high susceptibility analog modulation achievable in “thresholdless antiferroelectric” FLC devices. Recent work from the **Clark** labs has shown that all of the considerable literature in the field has been mistaken. The analog, so called “V-shaped switching” does not have anything to do with antiferroelectricity.<sup>[2]</sup>

Rather, this valuable effect occurs in SmC\* cells with special alignment conditions. Of particular importance is the insulating character of the alignment layers, which enable the reorientation of the SmC\* polarization to completely screen applied electric field.<sup>[3]</sup> The Boulder group insights into the origins of the effect have already led to the discovery of new V-shaped switching materials<sup>[4]</sup>

with extremely promising properties for incorporation into beam-steering devices, among others.

A main-chain NLOP of sideways-dimer mesogenic units (negative birefringence) which can be pulled into robust fibers where the polarization is normal to the fiber axis, has been synthesized by **Walba** using ADMET polymerization of a mesogenic diene. X-ray diffraction shows that the smectic layering is highly ordered with the layer normal parallel to the fiber axis. This enables a detailed understanding of the LC structure of the fibers.<sup>[5]</sup>

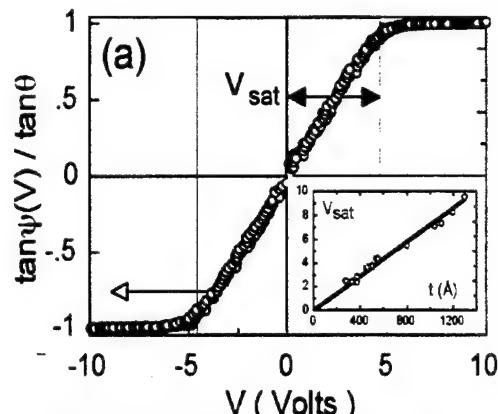


Figure 5. E-field-induced rotation of the optic axis in a SmC\* analog SSFLC cell. Sufficiently high polarization and sufficiently thick insulating alignment layers combine to make the cell exhibit analog EO, with a saturation voltage  $V_{sat}$  that depends on the alignment layer thickness,  $t$  (inset).

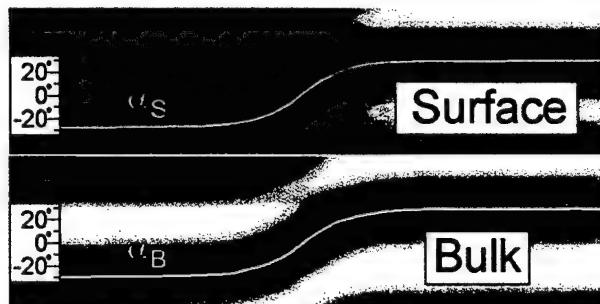


Figure 6. In this regime, bulk and surface molecular orientation, measured respectively by polarized transmission and reflection optical microscopy, are essentially identical, evidence for the polarization charge stiffening of the molecular orientation field. Clark's electrostatic model accounts for these observations.

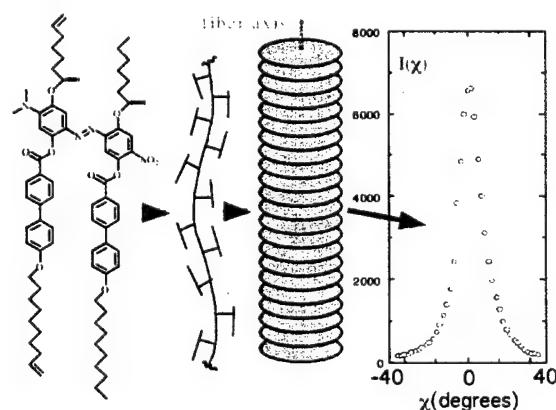
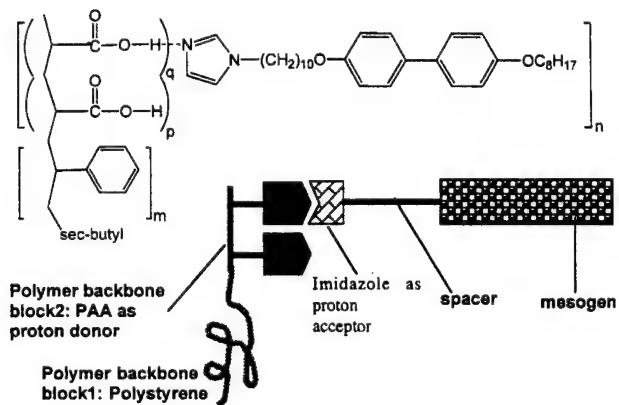


Figure 7. Main chain polymer of chiral side-by-side twins connected by a relatively high  $\beta$  azo group. The oligomers of this material can be pulled into fibers of a few  $\mu\text{m}$  diameter, which x-ray diffraction shows have smectic layers well aligned normal to the fiber axis. The layer spacing indicates that the phase is a SmC\*.

#### C.4 Hydrogen Bond Attachment of Side-Groups to SGLCP Block Copolymers: Cornell University

Block copolymers are gaining more and more attention both for fundamental research and for industrial applications due to their nanoscale microstructures and the capability of combining many desired properties into a single molecule. The side-group modified liquid crystalline block copolymers (SGLCBCP) have been investigated recently not only because of their specific microphase structures but also the advanced applications made possible by liquid crystallinity, for example, microphase stabilized ferroelectric liquid crystals. Though the covalently bonded SGLCBCPs possess interesting properties, there are still limitations due to their complex synthesis and the slow response. Instead, *hydrogen bonding* may offer an easier way to modify composition and the possibility of increasing the switching response speed since the hydrogen bonds are strong enough to form stable links between the polymer backbone and the side groups, but not so strong as to hinder mobility of the side groups. This approach provides a route to fine-tune the volume ratio between the two blocks by addition of the desired amounts of side groups and to tune the properties (e.g. refractive index) of the LC block by adding the additional moieties. The combination of a periodic nanostructure and liquid crystallinity offers us an exciting approach to make photonic band gap (PBG) materials that could be very useful in the communication industry.

To accomplish our goal for making compositionally tunable photonic bandgap (PBG) materials in the visible (VIS) and near IR ranges, **Ober** used high molecular weight poly(styrene-*block*-acrylic acid) as the polymer backbone with poly(acrylic acid) block functions as the proton acceptors and the side groups with imidazole or pyridine groups at one end of the mesogenic molecules as the proton donors. For the polymers, we have already synthesized P(S-*b*-AA) with several different molecular weights via the hydrolysis of anionically polymerized poly(styrene-*b*-*t*-butylacrylate). The very high MW P(S-*b*-tBA) [310K-115K] film shows blue color and a lamellar morphology, which means this MW is high enough to form a PBG film in the VIS wavelength range after modification of the polymer. Narrow MWD of the polymer is important for the formation of desirable periodic structures or morphologies, otherwise, the PBG properties won't be observed even for high MW polymers. To prove the H-bonded SGLCBCP is a homogeneous system without macrophase separation and periodic nanostructure after blending of polymer backbone and mesogens, we started from the simple mesogen (Fig. 8) and smaller MW P(S-*b*-AA).



Polarized optical microscopy and DSC studies prove the homogeneity of the blends with several different blend ratios while TEM studies show the high regularity of the morphology.

Moreover, we observed that the blend may form some complex morphologies such as H-bonded

Figure 8. Chemical structures and components of H-bonded SGLCBCP.

layers located in lamellae (Fig. 9) which was not seen in covalently bonded SGLCBCP systems. However, as polymer MW goes up, immiscibility increases, and the blends have a tendency to macrophase separate when the blend ratio (side group/acid group on the backbone) is larger than 0.8. To approach a primary goal of the project, an electric field switchable PBG mirror, the mesogens have been designed to possess strong dipole moment. Molecules having chiral centers or cyano groups have been synthesized and the switching study of the blend of PAA homopolymer and the mesogens is under investigation. Recent results show it is indeed possible to electrically switch the photonic bandgap properties of these blends using AC electric fields.

### C.5 Control of Alignment and Band-Gap Structures in LCs:

Kent State University

The main efforts during the MURI have been directed at understanding:

1. the dynamics of photoinduced reorientation and photobuffing
2. mirrorless lasing in cholesteric liquid crystalline materials, and
3. the study of the optomechanical response of liquid crystalline elastomers.

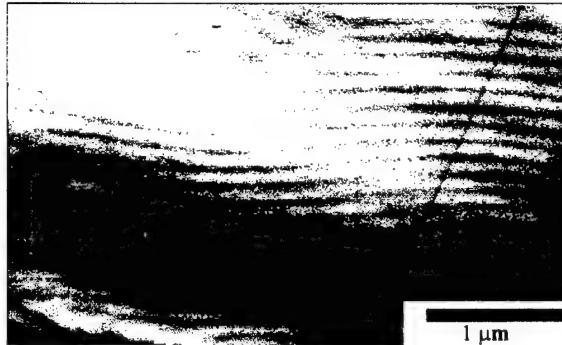


Figure 9. TEM image (Thomas) of one-dimensional lamellar morphology of P(S-b-MAA)/0.60M LC. The dark areas correspond to the MAA-LC domains.

Both experimental and theoretical work has been carried out by **Palffy-Muhoray** to probe the mechanism of light induced reorientation in liquid crystals. This included the measurement of optical nonlinearities in dyed liquid crystals, and the measurement photoinduced anisotropy in photosensitive alignment layers. The results were interpreted in terms of a generalized Fokker-Planck model.

Cholesteric liquid crystals are self-assembled photonic band-gap materials. The band structure gives rise to distributed cavity effects which allow population inversion in optically pumped samples, and mirrorless lasing. Fluorescent emission and lasing have been studied in low molecular weight liquid crystals, and in free standing liquid crystalline polymers and elastomers.

Recently, the optomechanical response of liquid crystalline elastomers has been studied. The dynamic response of azo-dye doped nematic elastomers has been characterized as function of irradiation intensity, wavelength, and dye concentration. The anomalous photoinduced reorientation of dye-doped liquid crystals, where light reorients the director against an elastic restoring torque essentially without the transfer of angular momentum, has presented a formidable puzzle to our understanding of light-matter interactions. Understanding the underlying mechanism is not only essential to our fundamental understanding, but is of key importance for the effective photobuffing of alignment layers needed in displays and other liquid crystal electro-optic devices.

It has been shown by the Kent group that the reorientation occurs via an orientational Brownian ratchet mechanism, where the dye molecules act as rotors of a light-driven molecular motor<sup>[6]</sup>. The process can be modeled via a Fokker-Planck description, comparison of experiment and simulation is shown below.

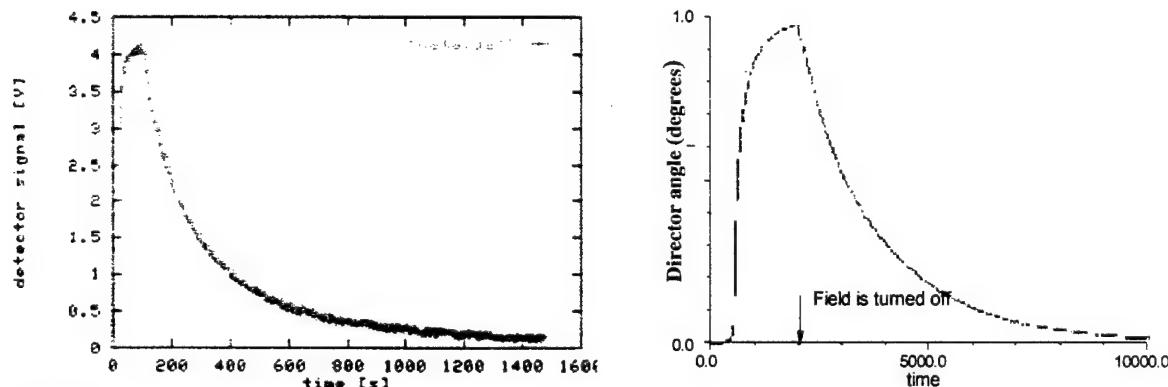


Figure 10. Onset and decay of photoinduced twist: experiment and simulation.

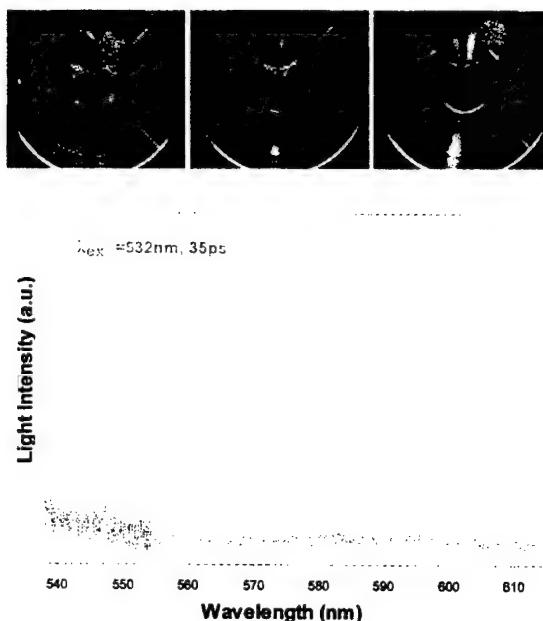


Figure 11. Cholesteric elastomer under biaxial stretch. The colors show the shift of the reflection band above, the shift of laser lines is shown below.

Together with **Clark**, information has been obtained on the orientational distribution function of the photoaligned dye<sup>[7]</sup>. Photoalignment has also been demonstrated in alignment layers incorporating the new two-photon azo-dyes from **Marder**.

Cholesteric liquid crystals are periodic dielectric structures and hence self-assembled photonic bandgap materials. Due to distributed cavity effects, in optically pumped samples, population inversion can occur, and above a threshold, mirrorless lasing. The Kent group has unambiguously demonstrated mirrorless lasing, for the first time, in samples of low molecular weight liquid crystals, in free standing liquid crystalline polymer films and in liquid crystalline elastomers<sup>[8]</sup>. The observed thresholds are typically low, in the nJ range, with linewidths of 3A and light to light efficiency near 20%. Since the optical properties of liquid crystalline elastomers can be changed by mechanical strain, lasing can be tuned by stretching these samples. The shift of the reflection band and of the laser line at the band edge in a cholesteric liquid single crystal elastomer is shown in Fig. 11.

Liquid crystal elastomers are exciting new responsive materials, whose physical properties are greatly influenced by the coupling between mechanical strain and orientational order. Changing the order parameter in these materials results in mechanical strain and change in the macroscopic configuration. The order parameter may be changed if the sample is irradiated by light; either due to heating due to absorption, due to a direct optical torque on the mesogens, or by an indirect optical torque via a ratchet mechanism. Very recently, the optomechanical response of nematic elastomers doped with an azo dye has been studied. Under laser illumination, the elastomer samples showed remarkable large mechanical deformations on very fast timescales.

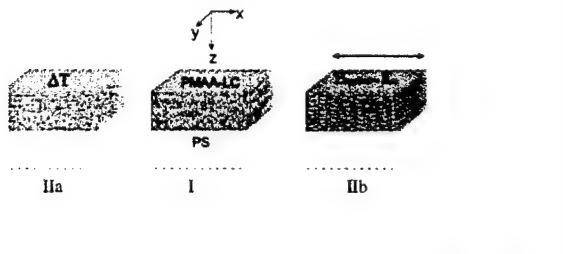


Figure 12a

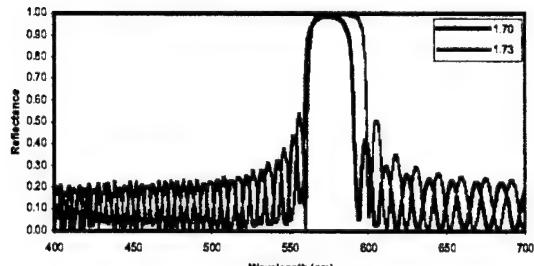


Figure 12b

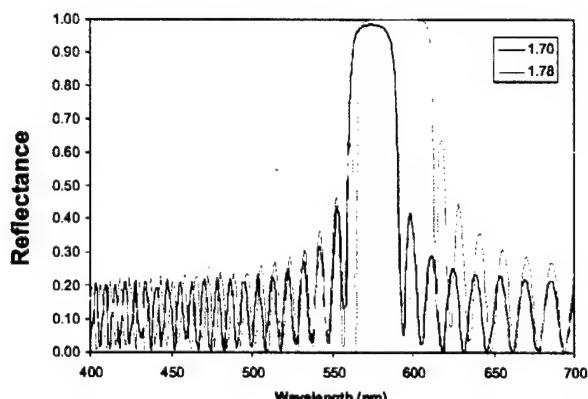


Figure 12c

**Figure 12:** a. Schematic of one repeat unit in the 1D self-assembled photonic band gap material. The material starts off with the LC layers parallel to the lamellae and perpendicular to the propagation direction,  $z$ . The optical properties of the state I can be changed using temperature or an electric field, leading to states IIa and IIb. b. Thermal randomization increases the effective  $n_{PMAA-LC}$  to 1.73 in state IIa, causing a red-shift in the reflectance band. c. Electric field reorientation of the LC layers increases the effective  $n_{PMAA-LC}$  to 1.78 in IIb.

The main objective was to fabricate a self assembled tunable optical switch in the visible using block copolymers with side chain liquid crystalline blocks. This task built upon the knowledge gained in the early years of the MURI in learning how to control the morphology of liquid crystalline polymers and on an understanding of simple 1D periodic optical systems. Hydrogen bonding was used to deliberately induce the formation of a liquid crystalline mesophase in one block of a suitable coil-coil diblock copolymer host. The incorporation of liquid crystallinity in a block copolymer results in an active material that can be used in electro-optic devices. As described above, Ober synthesized using anionic polymerization and hydrogen bonding a side group liquid crystalline diblock copolymer (LC-BCP) with a temperature dependent, limited photonic band gap in the visible. The P(S-b-MAA/LC) self assembles by simple solvent casting into a 1D

lamellar microdomain structure with a 175 nm period (Fig. 13). The as-formed structure exhibits an optical stop band in the green (Fig. 14a). Tunability of this structure is then shown by thermally inducing changes in the refractive index of the LC layers via alteration of the order parameter of the mesogens. The center of the stop band can be reversibly red shifted by approximately 10 nm for a change of 50°C (Fig. 15). From simulations it is possible to identify relevant criteria (refractive indices, mesogen orientation, anchoring conditions and microdomain geometry) that are useful in the design of LC-BCP material systems to achieve particular optical properties.

In addition to the need to provide a large difference in the respective dielectric constants of the materials comprising the photonic crystal, it is highly desirable to utilize materials whose index of refraction may be tailored and thus afford tunable photonic crystals. Several approaches to tunability have been explored, one route is to use optical pumping to create free charge carriers in a semiconductor<sup>[9]</sup>, another is to trigger a change in the lattice spacing of a colloidal crystal gel by for example, pH, temperature, ionic strength etc<sup>[10, 11]</sup>, another is to mechanically deform the lattice<sup>[12]</sup>, and another is to infiltrate the photonic crystal with a liquid crystal<sup>[13-16]</sup>. Both heat and electric fields can be used to dynamically manipulate the index contrast presented to incident polarized light by a periodic LC BCP photonic crystal. For initial work, we chose the simplest microdomain structure, namely the 1D periodic lamellar structure with alternating layers in our case of poly(styrene) and poly(methacrylic acid-LC), with the LC-containing layers displaying a smectic structure with homeotropic boundary condition as depicted schematically in structure I of Fig. 12a. Poly(styrene) is isotropic with an index in the visible of 1.59, poly(methacrylic acid) is also isotropic with an index of 1.45 and the imidazole mesogen is assumed to be uniaxial with an index of 1.80 in the isotropic regime. Thus, at temperatures below the smectic to isotropic transition, light incident along z, polarized along x, experiences an index of  $n_A = n_{PS}$  in the poly(styrene) layers and  $n_B = (\varphi_{LC} n_o^2 + (1 - \varphi_{LC}) n_{PMMA}^2)^{1/2}$  in the poly(methacrylic acid-LC) layers where  $n_{PMMA}$  is the index of the poly(methacrylic acid) backbone and  $n_o$  is the ordinary refractive index of the mesogens. On thermal clearing of the LC, the sample will have morphology as depicted in structure IIa. For reasonable values of birefringence for the organic mesogen,  $\Delta n = n_e - n_o \sim 0.07 - 0.20$ , we can expect a change in the index of B layers in the system upon thermal clearing of the liquid crystalline state of roughly  $\Delta n_B = n_B - n_B \sim 0.02 - 0.05$  for  $\varphi_{mesogen} \sim 0.7 - 0.8$ . Calculations using the Berreman transfer matrix method<sup>[17]</sup> for a 50 bi-layer stack predict a broadening and shifting of the stop-band towards the red with a corresponding increase in the reflectivity (Fig. 12b). Alternatively, the index can be changed via an applied electric field by reversibly aligning either the ordinary or extraordinary components of the mesogen's refractive index parallel to the oscillation of the electric field of the incoming light. Assuming a positive dielectric susceptibility, an applied electric field  $\bar{E}_x$  could realign the mesogens along the x-axis so that for incoming light with electric field vector oscillating along x (structure IIb), the index in the B layers is now given by  $n_B = (\varphi_{mesogen} n_e^2 + (1 - \varphi_{LC}) n_{PMMA}^2)^{1/2}$ . In this case, a greater effect would be produced,  $\Delta n_B = n_B - n_B \sim 0.06 - 0.16$ , using the same range of values for the mesogen birefringence ( $\Delta n$ ) and volume fraction ( $\varphi_{mesogen}$ ) given above (Fig. 12c). The typically high electric fields (30-300 V/μm) necessary for LC reorientation are usually realized with reasonable voltages by using a thin

sample. However, the inherently layered geometry with homeotropic anchoring of the mesogens in our present material requires that a potential difference be placed across the usually large sample dimension along the x direction. In our initial experimental work, we pursued the thermal approach to index manipulation.

A P(S-b-AA) diblock copolymer having a 500k g/mol PS block and a 96k g/mol PMAA block was synthesized as described above and blended varying amounts of the H-bonding mesogen to form the SG-BCP (Fig. 8). Films were cast from solution at 2-5 wt.% in THF. Solvent removal was conducted by evaporation over 18 hours at room temperature (22-24 °C) in a THF vapor saturated atmosphere to produce films approximately 5 microns to 200 microns thick. Films were subsequently dried under vacuum for 12 hours. The films were characterized thermally using differential scanning calorimetry (DSC) and optically using polarized optical microscopy (POM) and transmission/reflectance spectrophotometry. Microstructures were observed using small angle x-ray scattering (SAXS), and transmission electron microscopy (TEM).

The neat diblock copolymer, P(S-b-MAA) forms hexagonally packed cylinders of poly(methacrylic acid) embedded in a poly(styrene) matrix, as deduced by TEM and SAXS. The average cylinder-cylinder spacing was 120 nm and simple cast films of the polymer are clear and colorless. The mesogen is a white powder with a melting point of 46 °C. It is approximately 30 Å in length and found by SAXS to have a layer period of 54 Å, suggesting a partially interdigitated bilayer arrangement.

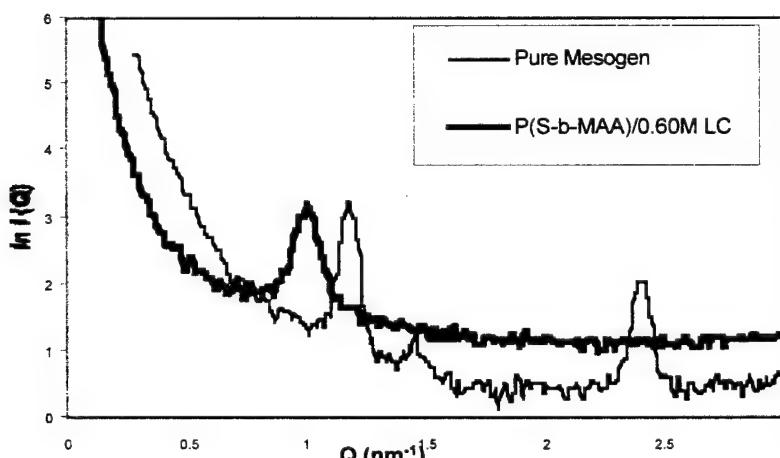


Figure 13. SAXS from P(S-b-MAA)/0.60M LC and the pure mesogen.

transition in the LC-BCP occurs over a broad temperature range, from about 65-85 °C. The heat of transition (normalized to the LC block content) on the initial heating is 10.7 J/g whereas it is 3.2 J/g on second and subsequent heatings. The disparity in the enthalpies suggests that the first passage through the clearing point involves a transition from an LC structure with a higher degree of order as compared to the second and subsequent transitions. The morphology which is initially established

P(S-b-MAA) forms single-phase films over the composition range studied, from 0.10 to 0.80 molar ratio of mesogen to acrylic acid repeat units. SAXS and DSC confirmed the formation of a liquid crystalline phase within the block copolymer that exhibited distinctive structural and thermal characteristics as compared to those of the pure mesogen. The smectic to isotropic

during solvent removal becomes inaccessible to the system during the subsequent thermal cycles in the melt state. The transition enthalpy of 3.2 J/g is on the same order of magnitude as observed in covalently bound systems previously studied<sup>[18]</sup>. Thermal treatments below about 110 °C do not appear to cause noticeable macrophase separation of the mesogen from the block copolymer host – there is no evidence of pure mesogen signatures in the DSC and SAXS of samples which have undergone heating up to 110 °C for short times. Beyond 110°C, accelerating anhydride formation along the methacrylic acid backbone depletes mesogens from the polymer resulting in their macrophase separation from the polymer chain and the production of turbidity in the films.

P(S-b-MAA/LC) films less than 200 microns thick were clear and appeared blue to green depending on the particular LC content and the viewing angle. In particular, at 0.60 molar ratio (0.60M) and for normal incidence, green films were produced, as shown in the photograph in Fig. 14a. Heating into the isotropic regime gives a film with red-orange color in reflection (Fig. 14b). Bright field TEM images of cross sections of the films (see Fig. 9) indicate that the LC BCP self-assembled into a lamellar structure, with a layer period of approximately 165 nm with the lamellae preferentially oriented parallel to the surface of the glass vial in which the samples were cast. The dark areas in the unstained TEM image correspond to more electron dense poly(methacrylic acid-LC) domains.

SAXS patterns obtained with x-rays incident parallel to the film surface (cross-sectional) confirm the layering of the domains parallel to the substrate surface with quite long range order (6<sup>th</sup> order reflections are readily observed). A lamellar period of 175 nm is calculated using the third and

higher orders of the lamellar reflections, and is in good agreement with the period derived by the TEM inspection. Order parameters ( $P_2 = \langle 3\cos^2 \alpha - 1 \rangle / 2$ , the second coefficient of the orientation distribution function) as high as 0.77 for the lamellae and 0.55 for the smectic layers were derived in the manner of Windle and Mitchell<sup>[19]</sup> from data taken from a particularly well aligned and large-grained sample. The smectic order parameter was measured as a function of temperature. Starting from 0.29 at 40 °C, it decreased and increased reversibly by a factor of 2 on thermal cycling to 70 °C and back to 40 °C.



Figure 14a



Figure 14b

Figure 14. Photographs of pieces of the reflective polymer, field of view is 1x2 mm. The cracks were accidentally introduced during sample removal.  
a. Sample at 30 °C. b. Sample at 80 °C

We investigated the temperature dependence of the optical properties of this self-assembled dielectric stack by obtaining the normal incidence transmission spectrum of 200 micron thick samples illuminated with an incandescent white light source through a plane polarizer using a hot stage mounted in an optical microscope with a heating and cooling rate of 10 °C /min. Heating from room temperature up into, but not beyond the transition region gave a small, reversible red-shift of the minimum of the sample transmittance (e.g., a 9 nm shift from 560 nm to 569 nm occurs over the interval from 40 °C to 70 °C, accompanied by a decrease in the transmitted intensity from about 72% to 60%, i.e. the sample became more reflective). Heating beyond the smectic to isotropic transition, to 90 °C, produces a substantial red-shift of 40nm in the minimum of the sample transmittance without change in the magnitude of the transmittance. However, these effects are no longer reversible – upon cooling back to 40 °C from 90 °C the minimum remained centered at 600 nm (vs. the 560 nm initial position).

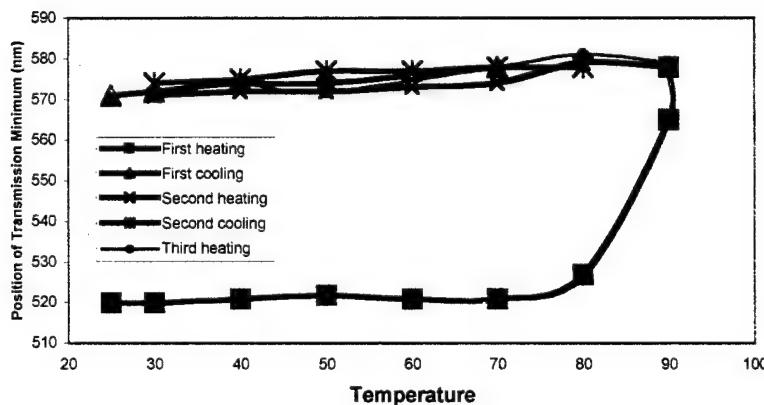


Figure 15. Position of the transmission as a function of temperature shows that a substantial change in the reflection band occurs with the smectic-to-isotropic transition; however, this change is irreversible with the existing materials.

film about 9 microns thick) for various mesogen orientations show that the case in which the index of the PS domain is matched to  $n_e$  of the PMAA-LC domain results in the material functioning as a *polarizing filter*, as TE modes within the band gap are stopped whilst TM modes are allowed to propagate. From simulations such as these, we are able to identify relevant criteria (refractive indices, mesogen orientation, anchoring conditions and microdomain geometry) that we can use in the design of our material system to achieve particular properties.

The experimental results agree qualitatively with those predicted by our simulations, which anticipate an increase in the efficiency of the stop band as observed by the deepening of the transmission dip, and a small shift of the stop band to higher wavelengths. This is expected due to the increase in index contrast between the layers. The gradual change in transmission is due to a similarly gradual transition in the order parameter of the mesogens on melting. The small, broad second heating transition centered at 78 °C and the lack of an observable exotherm on cooling

The simulated normal incidence reflectance for three ideal structural states (I, IIa, IIb) is plotted in Figs. 12b and 12c. Since experimental samples exhibit layer misorientation as well as a relatively low and a temperature dependent order parameter of the mesogens, it is informative to compute the reflectance as a function of incident angle for TE and TM polarizations for suitable choices of refractive indices. Simulations of the reflectance calculated using 50 periods (corresponding to a

suggest that the packing of the mesogens in the original “as-cast” state is quite different than in states achieved by subsequent thermal cycling of the material. The significant rate dependence of the enthalpy of the transition - e.g. cooling faster than 20 °C /min. in the DSC resulted in the absence of the peak in a subsequent heating experiment, also suggests that the reorganization of the mesogens is relatively slow. It is very likely that the morphology space accessible to the sample in the solid state is very different than that it experienced in the presence of solvent, such as when initially produced by casting. Path dependent morphologies are an important feature of liquid crystalline block copolymers<sup>[18]</sup>.

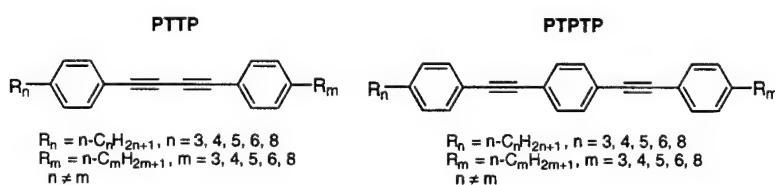
### C.7 High birefringence LCs and Modeling of Orientational Interactions: University of Southern California

Dalton's research has been focused on three tasks:

1. preparation of new polar tolane liquid crystals for evaluation by Dr. Shin-Tson Wu of HRL Laboratories,
2. development of new theory to better understand order achieved in LC materials characterized by intermolecular electronic electrostatic interactions as well as by shape effects, and
3. attempts to achieve higher order in phase-separation LC systems by exploitation of hydrogen bonding.

The first objective has been quite successful. New nematic LC materials have been prepared with improved properties. A patent application entitled “Polar Tolane Liquid Crystals” has been prepared. The second objective has likewise been advanced. Improved theory has been developed and demonstrated for the calculation of phase diagrams. The results in the third area of activity has been interesting and unanticipated. Phase separation in ABCA' block copolymers has been observed by electron microscopy. However, the morphology has been observed to be more complicated than anticipated.

We have synthesized a series of asymmetric diphenyl-diacetylene liquid crystals (**PTTP**), which provide a useful electro-optic medium for modulating infrared radiation and high-speed light shutters due to their high birefringence ( $\Delta n$ ) and relatively low viscosity. In particular, these materials have been utilized for device applications by Hughes Research Laboratories and by Raytheon. Clearly, there is a need to improve the birefringence of this class of nematic LC materials leading us to develop the **PTPTP** family of LC materials.



TPTP incorporates one more phenyl group into PTTP backbone, which increased the birefringence due to the conjugation length increase of the long axis. However this modi-

fication changed the physical properties of the liquid crystals as well, such as higher melting temperature. The asymmetric alkyl chains helped to lower melting temperature significantly. Therefore, we synthesized the PTPTP homologues with different asymmetric alkyl terminal groups to explore the highest  $\Delta n$  that can be obtained while keeping melting temperature within an

acceptable range. We started from PTPTP-48, -46 and -68, compounds which should give us birefringence around 0.46 in the visible region, compared to 0.40 for PTTP liquid crystal materials.

Because p-hexyl benzaldehyde or p-hexyl benzaldehyde diethyl acetal was not commercially available, we used reduction of acid chloride with lithium tri-t-butoxyaluminohydride to produce the p-hexylbenzaldehyde. The reactions from p-hexylbenzaldehyde to corresponding PTPTP are similar to above procedures. These materials were provided to **Wu** for characterization (see S. T. Wu, C. S. Hsu, K. F. Shyu, Y. Y. Chuang, H. B. Cheng, Z. Chai, G. Day, L. Guo and L. R. Dalton, "High Birefringence Bis-Tolane Liquid Crystals for Display Applications," *SID Tech. Digest* **30**, 706-9, 1999). A patent has recently been filed by Hughes dealing with materials synthesized during the past two years.

**C.8 Microfabrication of Switchable LC grating Devices:** Univ. of Arizona, Kent State and Cornell

**Perry, Marder, and Palffy-Muhoray**, in collaboration with **Bunning** (AFRL/MLPJ), have explored the use of two-photon microlithography for fabricating electrically switchable liquid-crystal-filled gratings (LCFGs). LCFGs may be useful in several optical applications, including electro-optic switching, free-space optical interconnects, and anti-jamming. Single layer grating structures (Fig. 10 of Laser Hardening section) were fabricated on ITO coated substrates, treated with LC alignment layers, then packaged into cells and back-filled with 5CB and 7CB/5CB (4:1) mixtures. The packaged devices act as electrically switchable thin diffraction gratings (Fig. 10 of Laser Hardening section).<sup>[20]</sup> 3D structures have also been fabricated and back-filled with LCs. Devices of this type should have application for 3-5  $\mu\text{m}$  beam steering.

**Perry, Marder, and Ober** are also exploring the use of positive-tone 3D microlithography for fabricating switchable microoptical devices. **Marder** and **Perry** have developed the high-sensitivity two-photon photoacid generator **BSB-S<sub>2</sub>** (described in the Laser Hardening section), which can be used for patterning acid-sensitive materials. **Ober**'s group has developed **THPMA-MMA**, a solid-state chemically amplified resist based on acid-cleavable side-chain ester groups (structure given in the Laser Hardening section). The initiator and polymer have been combined to form a two-photon-patternable resist and have been used for high-fidelity positive-tone 3D microfabrication of grating structures (Fig. 13 of Laser Hardening section).<sup>[21]</sup> The grating channels can be back-filled with liquids, including liquid crystals. They are currently investigating the use of this material system for fabricating more complicated switchable microoptical structures.

### **C.9 Summary**

The advances in materials development under the LC MURI may play central roles in the paradigm shifts underway in display technology. Analog FLCs and new strategies for fabricating devices with the LCs that exhibit thresholdless FLC electro-optic response promise to greatly enhance the performance of FLC displays and open unprecedented FLC applications such as beam steering where analog response is vital. New electron conducting organic compounds address challenges in OLED technologies. Mirrorless lasing in cholesterics may open new strategies for control of color and directionality in emissive displays. Thermally reversible LC gels present opportunities for facile coating and control of orientation in web-based processing of LCDs and LC-based optical elements.

(compensators, filters and polarizers). In addition, new LCs and additives developed under the MURI are expanding the spectral range and enhancing the performance of existing LCDs. Beyond displays, the new materials, fabrication strategies and devices explored by the MURI team feed into sensor, actuator and signal processing technologies.

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### **III. Laser Hardening Thrust**

Joseph Perry, University of Arizona -- Thrust leader

Robert Grubbs, California Institute of Technology

Seth Marder, University of Arizona

Chris Ober, Cornell University

Peter Palffy-Muhoray, Kent State University

Larry Dalton, University of Southern California

#### **A. Overview of Thrust**

The Laser Hardening Thrust of the AFOSR Liquid Crystal MURI has investigated liquid crystal (LC) materials, mechanisms and processes which have potential for applications in laser hardening. The objectives of this thrust were to: 1) develop new liquid crystal (LC) materials for laser hardening with enhanced nonlinear optical responses, 2) create new LC polymeric materials with controllable and stable internal order for advanced nonlinear optical and electro-optical components, and 3) to reduce the switching voltage and switching times of LC materials.

Over the five year period of the center's existence, advances have been made in the development of new electron deficient discotic liquid crystals, electrically switchable LCs with improved transparency, the fabrication of LC-filled switchable gratings, and in improving understanding of the mechanisms of enhanced nonlinear absorption in doped LC composites by way of two-photon photoconductivity studies. These advances have been made possible by interactions among MURI participants, and outside of the MURI with both industrial and government lab researchers. A summary of these highlights is given below:

##### *1. Discotic LCs for Electron Transport: Marder, Clark, Kornfield*

Discotic liquid crystal based upon electron deficient molecules have been synthesized and have been shown to form hexagonal columnar phases that can be homeotropically aligned and which feature high charge mobility. A provisional patent has been submitted on these materials.

##### *2. Liquid Crystal Filled Switchable Gratings:*

**Perry, Ober, Marder, Palffy, Clark, Bunning (AFRL)**

Low voltage switching of the diffraction efficiency of liquid crystal filled gratings fabricated by two-photon lithography has been demonstrated. Improvements in the fabrication steps and device packaging procedures have yielded devices with reduced background scatter and reproducible switching behavior. Highly efficient two-photon photoacid generators and optimized chemically amplified solid-state resists were developed and applied to fabrication grating structures in a positive-tone resist composite. The results of these investigations are being published in *Science*.

**3. Mechanism of Enhanced Absorptive Nonlinearities in Two-Photon Dye Doped LC Materials:  
Perry, Marder, Palffy, Kornfield, Wu, Fleitz (AFRL)**

Two-photon photoconductivity studies have shown that charge carriers are generated by two-photon excitation of two-photon dye doped cyanobiphenyl (CB) LCs and that this effect is amplified by the LC order. These investigations have provided a clear indication that the enhanced nonlinear absorption in these systems results because the ordered LC matrix promotes two-photon generation of absorbing radical ions.

**4. High-dipole LC additives for low- $V_{th}$  switching: Marder, Wu, Bunning (AFRL)**

Colorless molecules with dielectric anisotropy greater than 50 have been synthesized and have been shown to lower the liquid crystal switching voltage,  $V_{th}$ . A joint Caltech/Hughes patent has been filed on these materials.

**5. New low-viscosity high-birefringence liquid crystals: Dalton, S.-T. Wu**

New low-viscosity high-birefringence liquid crystal materials based on phenyl-acetylenes and terphenyl mesogen cores have been synthesized and some of their physical properties have been examined.

## B. Efforts in PI Laboratories

### *University of Arizona*

**Marder.** In close collaboration with **S.-T. Wu**, we have designed and synthesized a series of colorless, acceptor-substituted, mono- and diyne-molecules, as high dielectric anisotropy dopants for use in lowering the operational voltage of LC compositions. This work has resulted in molecules that are transparent in the visible region of the spectrum and that lower the switching voltage of a range of liquid crystals and additionally lower the viscosity of the LC phase. A joint Caltech/Hughes patent has been filed on these materials. We have developed new two-photon active chromophores that can be used for photobuffing of alignment layers in LC cells. We have also created a completely new class of discotic liquid crystals that are electron deficient.

**Perry.** Our efforts have included 1) investigation of the mechanism of the enhanced nonlinear absorptive properties of two-photon dye doped LCs using two-photon photoconductivity measurements, optical limiting measurements, and time-resolved spectroscopic characterization of the intermediates generated subsequent to one- and two-photon excitation of the dye-doped LC medium; and 2) fabrication and characterization of LC filled grating structures produced using two-photon microfabrication. Extensive spectroscopic and photoconduction studies, with Palffy-Muhoray, have been performed to develop an understanding of the mechanism of enhanced nonlinear absorption in bis-donor two-photon dye/LC guest-host systems. These studies have produced definitive evidence showing that strongly absorbing radical ions generated by two-photon excitation are responsible for the enhancement. In collaboration with **Palffy-Muhoray** and **Bunning** (AFRL), we have fabricated LC filled 2D grating structures and have been characterizing their switchable diffraction properties. In collaboration with **Ober** and **Marder**, we have developed a new positive-tone chemically amplified solid-state resist incorporating a high-efficiency two-photon photoacid generator. We have shown that this

material can be 3D-patterned rapidly and with low excitation power. Using the solid-state resist, we have fabricated 3D grating structures and have back-filled them with liquid crystal materials. Further studies are continuing with this system, including optical characterization of the LC-filled positive-resist gratings.

*Cornell University*

**Ober.** In collaboration with **Perry** and **Marder**, we have designed, synthesized and tested several acrylate resin systems for two-photon-initiated three-dimensional microfabrication. A side-chain cross-linkable polymer has been synthesized to serve as an additive in the pre-polymerization mixture. Initial tests suggested that efforts to optimize cross-linkable-bond content for better polymerization efficiency and volume shrinkage control were needed. A series of cross-linkable additives have been prepared that have a range of side-chain functionalization. These are currently being tested. We also investigated the possibility of two-photon microlithography based on a solid resin system comprised of chemically amplified photoresists and photoacid generators. Early test of this resin were negative as no photoacid generators were available that could be efficiently activated by two-photon excitation. **Marder** and **Perry** have designed and synthesized a photoacid generator based on a Donor- $\pi$ -Donor chromophore that can be efficiently two-photon activated. New chemically amplified resist formulation incorporating this photoacid generator have been found to be very effective for microlithography.

*Kent State University*

**Palffy-Muhoray.** Our research has focused on intensity dependent optical nonlinearities in orientationally ordered materials, with emphasis on 1) nanosecond response of pure and doped nematic liquid crystals, 2) optically induced reorientation of dichroic dyes in an orientationally ordered environment, 3) optical nonlinearities in binary mixtures of fluids, 4) theoretical issues involving linear and nonlinear light propagation, and 5) calculation of molecular properties. Our group has been fabricating various types of LC cells for optical and electro-optical studies and has made these cells available to other MURI groups. We have also been performing Z-scan measurements of refractive nonlinearities of two-photon dye doped CB LCs developed and studied in this MURI.

*University of Southern California*

**Dalton.** We have synthesized a series of asymmetric diphenyl-diacetylene (PTTP) liquid crystals (Scheme 1), which provide a useful electro-optic medium for modulating infrared radiation and high-speed light shutters due to their high birefringence ( $\Delta n$ ) and relatively low viscosity. In particular, these materials have been utilized for device applications by Hughes Research Laboratories and by Raytheon. Clearly, there is a need to improve the birefringence of this class of nematic LC materials leading us to develop the PTPTP family of LC materials.

### C. Accomplishments and New Findings

*University of Arizona / California Institute of Technology*

**Marder.** We have created a completely new class of discotic liquid crystals that are electron deficient. **Clark** and **Kornfield** have examined the phase behavior of these liquid crystalline materials by microscopy. The thermal behavior exhibited by microscopy is in agreement with that shown by differential scanning calorimetry. Several of the compounds show broad temperature ranges for LC phases in some case going down to room temperature. Microscopy on these materials on a substrate with an alignment layer exhibited no birefringence, indicating that the LCs form hexagonal columnar phases that can be homeotropically aligned. These dye have been sent to **George Malliaras** of Cornell University for time of flight measurements to measure electron mobilities. Mobilities on the discotic liquid crystals have been measured and are in the range of  $\text{cm}^2/\text{Vs}$ . These compounds have been incorporated into working organic light emitting diodes

We have developed some high dielectric compounds as colorless dopants for lowering the  $V_{th}$  of LC mixtures. These dopants possess a huge dielectric anisotropy. Adding ~3% of this dopant to an LC mixture is enough to see a dramatic reduction in  $V_{th}$  while keeping viscosity in the acceptable range. Several compounds (Fig. 1) have been synthesized and characterized whose molecular structures are shown below:

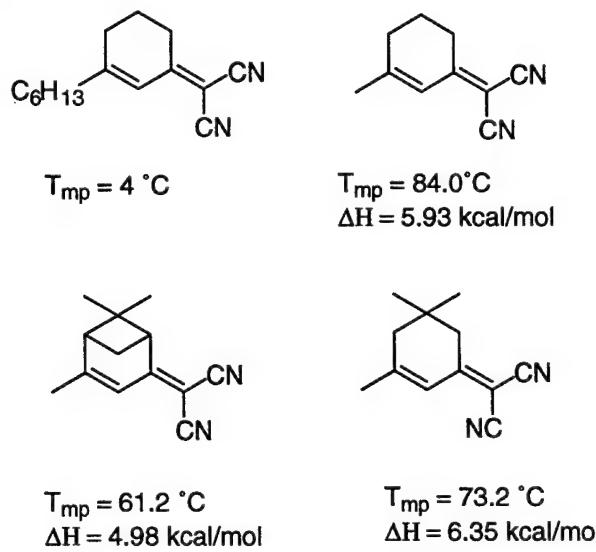


Figure 1. Compounds synthesised and tested as LC additives for lowering  $V_{th}$ .

As can be seen the molecules above have relatively low melting points and low heats of fusion. Our ability to tune these parameters is useful for controlling the ultimate solubility of the dyes in LCs In the figure below (left) it can be seen that it is possible to make completely colorless mixtures of dyes with large dielectric anisotropies and liquid crystals. Below right is shown the effect of adding a colored (a) and colorless (b) dopant to a high birefringence liquid crystal (PTTP). From the data below it was deduced that compound (b) had a dielectric anisotropy of > 50.

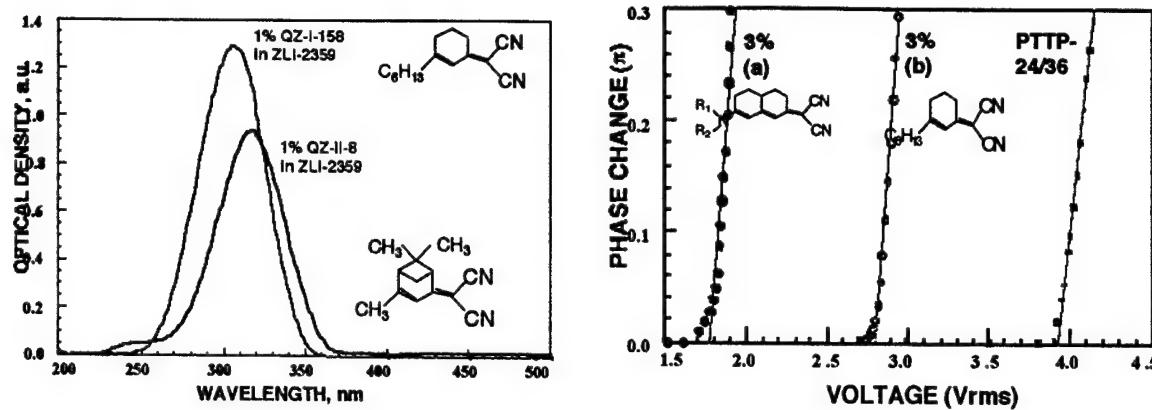


Figure 2. Left: Absorption spectrum of two LC-additives, QZ-I-158 and QZ-II-8; Right: Phase change versus applied voltage of three Additive/LC-composites.

The LC dopants and discotic liquid crystals have been transitioned to Bernard Kippelen for physical studies and incorporation into devices.

### *Cornell University*

**Ober.** Earlier work by **Perry** and **Marder** showed that 3D lithographic microfabrication resins used for producing LC-backfillable gratings suffered from shrinkage during the post-exposure solvent wash which led to deformation of the structure. The shrinkage effect is thought to result from extrusion of a polymer binder additive that is part of the microfabrication resin. In hopes of obtaining improved LC gratings, we synthesized an alternative "binder" based on a random copolymer of methyl methacrylate and 2-hydroxyethyl methacrylate (HEMA) and derivatized HEMA with acryloyl chloride to produce a solid linear polymer bearing cross-linkable acrylate side-groups. A particular merit of this system, relative to "binder" additives used previously, such as poly(styrene-co-acrylonitrile), is that the cross-linkable binder will become covalently bound to the cross-linked polymer matrix so that it cannot be extracted by the solvent developer during the solvent developing step. The composition of the resin we used to fabricate test microstructures was SR9008, SR368, crosslinkable polymer and a bis-donor bis(styryl)benzene two-photon absorbing dye from the University of Arizona in a wt.-ratio of 35.2: 34.5: 30.1: 0.2, respectively. Volume shrinkage was still observed in initial studies (Fig. 3). We then formulated new resins based on neat cross-linkable polymer additive. No structures could be produced with this resin under similar exposure conditions. In principle, in order to get polymerization in a solid state resin it is necessary for a cross-linkable group to have another monomer-group in its inner solvation shell. So based on the above observations, it seemed that the double bond concentration in this copolymer was too low for crosslinking to occur. We have since then synthesized a series of new co-polymers with higher double bond content, and these are currently being tested.

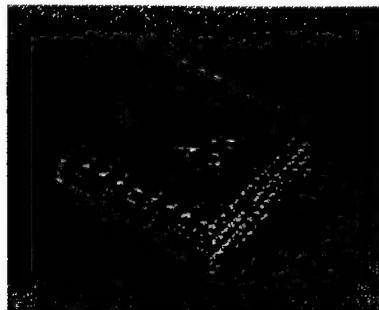


Figure 3

We have also worked on solid-state systems based on chemically amplified photoresists for microlithography. We have prepared random co-polymers of tetrahydropyranyl methacrylate and methyl methacrylate and methacrylic acid in a 40:57:3 ratios (Fig. 4). The material proved to be UV sensitive and photopatternable (Fig. 5) with triphenylsulfonium hexafluoroantimony as a photoacid generator (PAG) using a KrF excimer laser at Cornell Nanofabrication Facility (CNF). Use of this class of materials for microfabrication is described below.

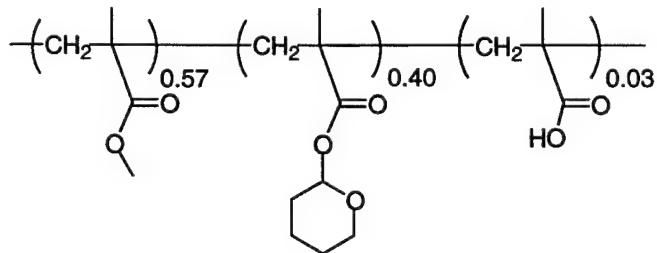


Figure 4

*University of Arizona*

**Perry.** In collaboration with **Marder, Palfy, Kornfield, Wu, and Fleitz** (AFRL), we have investigated the origin of the enhanced nonlinear absorption properties of two-photon dye/LC guest/host systems. A wide range of new guest host systems has been prepared, including biphenyl and *bis*(styryl)benzene based two-photon dyes. Nonlinear optical absorption experiments with 5-8 ns laser pulses at 600 nm, the peak wavelength of the nonlinear absorptive response of *bis*(dibutylamino)stilbene (BDAS) in toluene solution, were performed on the BDAS/7CB/5CB LC guest/host system. The results showed that the effective three-photon absorption cross section,  $\gamma$ , was enhanced by a factor of 22 compared to the same system in the isotropic state, indicating that the dominant enhancement mechanism depends on the local orientational order of the nematic state. Time- and wavelength-resolved photoinduced absorption measurements provided strong evidence

Figure 5



pointing to the photogeneration of radical ion charge carriers as the origin of the large photoinduced absorption.

Extensive wavelength and intensity dependent photoconductivity measurements were undertaken to assess the role of two-photon charge-carrier generation in the overall optical-limiting response. A quadratic intensity dependence was observed confirming that the charge carrier generation was due to two-photon absorption (Fig. 6). The photocurrent action spectrum shows a peak around 600 nm, consistent with the position of the peak two-photon absorption of BDAS (Fig. 7). These results provide compelling evidence that the enhanced nonlinear absorption properties of the BDAS/7CB/5CB LC guest/host system is due to generation of radical ion charge carriers with strong absorption at the pumping wavelength. These experimental results confirm that the observed enhancement is due to generation of absorbing charge carriers, whose overall yield is enhanced by the orientational order of the nematic LC host. These results imply that two-photon photorefractivity should be observable in these system and suggests possible photorefractive applications. Various compounds and LC cells have been sent to **Paul Fleitz (AFRL)** for evaluation.

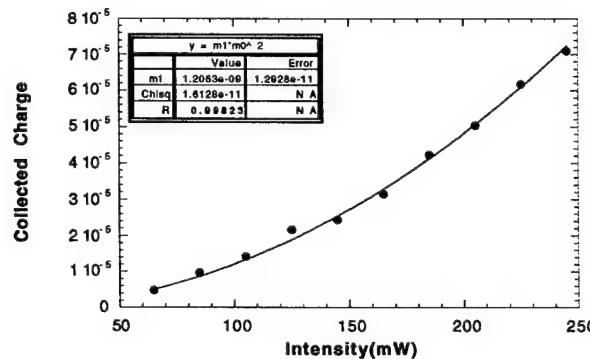


Figure 6. Intensity dependent photocurrent in BDAS doped CB LC showing a quadratic intensity dependence.

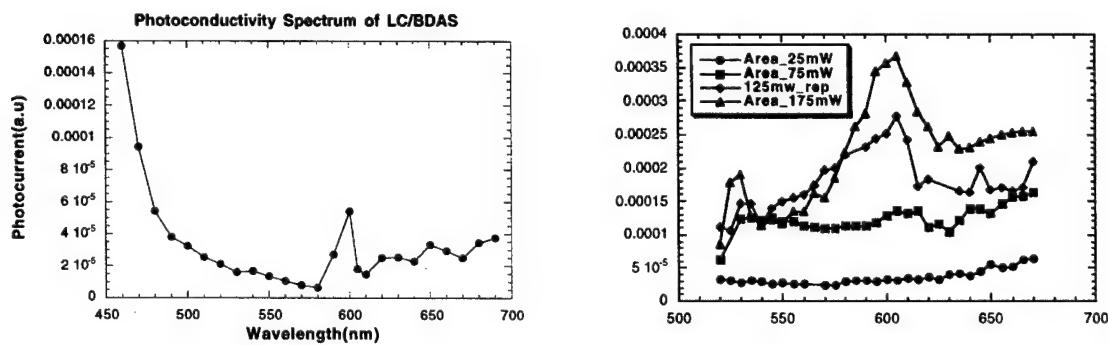


Figure 7. Two-photon photoconductivity action spectra of BDAS/LC guest/host system, Left: wide wavelength scan; Right: higher resolution scan at different intensities.

Systems of this type offer great promise for broad-band optical limiting, as a range of two-photon chromophores can be incorporated into the LC matrix to provide protection across the visible spectrum. Fig. 8 shows the two-photon absorption spectra of a series of D- $\pi$ -D chromophores, as well as some measurements of the effective two-photon cross-section that results due to two-photon excited-state absorption. Further two-photon photoconductivity studies have shown that D- $\pi$ -D chromophores with longer  $\pi$ -bridges, such as the bis(stryl)benzene chromophore of Fig. 8 also generate charge carriers upon excitation when solvated in cyanobiphenyl LC's. Thus, the mechanism of enhanced nonlinear absorption due to chromophore ordering and two-photon generation of strongly absorbing charge carriers appears to be general for this class of molecules.

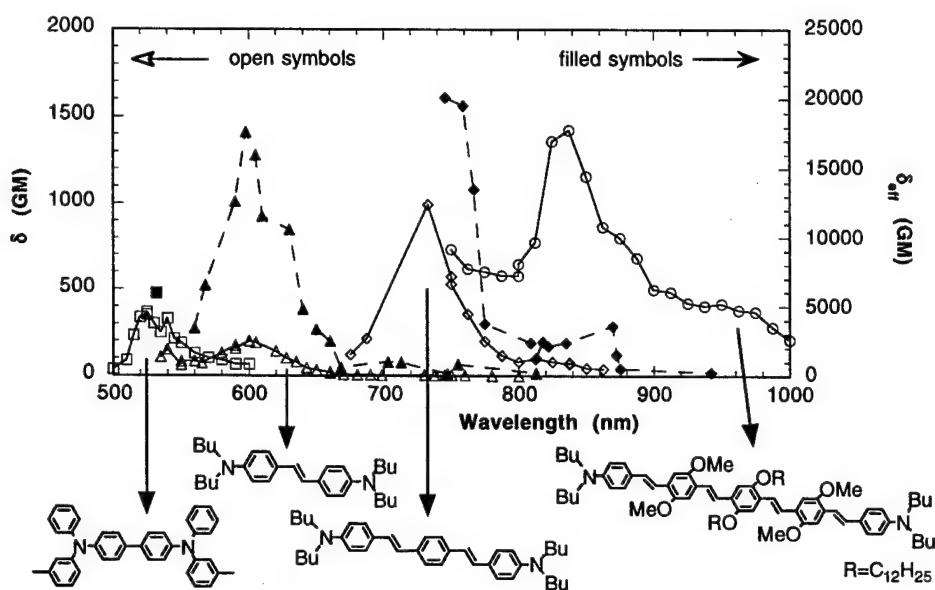


Figure 8. Two-photon spectra of a series of D- $\pi$ -D chromophores.

In collaboration with **Kornfield**, we have also examined the use of gel-forming two-photon chromophore/LC-polymer composites for optical limiting. LC gels are expected to damage at much higher fluences than solution or liquid-phase LC systems, and thus would offer enhanced performance. An LC-gel composite was formulated based on a blend of 5% of the LC-polymer MKLC (Fig. 9) into 5-cyanobiphenyl, to which was added the two-photon chromophore BDAS (6 wt.-%). The optical limiting performance (Fig. 9), indicates that relative to the BDAS/LC systems examined earlier, the LC-gel composite exhibits strong optical limiting with a reduction in the limiting threshold of only 40%. These studies offer further confirmation that in two-photon chromophore/LC composites, the persistent optical limiting effects result from hopping of charges through the ordered LC matrix, and not charge migration by mass transport. Materials of this type offer great promise for broad-band high damage threshold optical limiting.

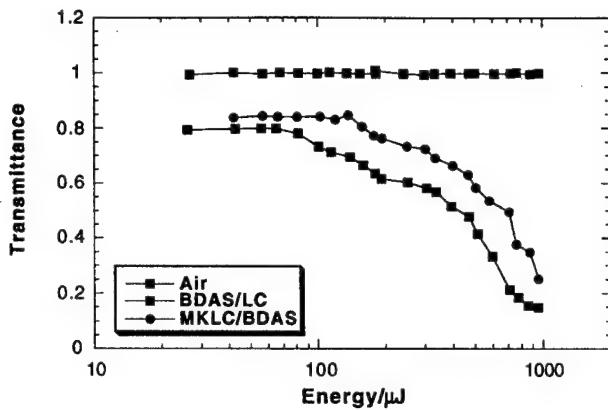
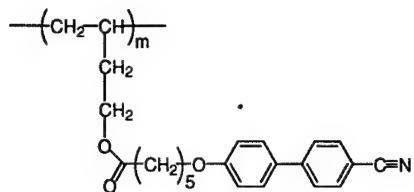


Figure 9. Left: The LC-polymer MKLC. Right: Optical limiting performance of a LC-gel composite consisting of 5%MKLC in 5CB with 6 wt.-% BDAS as the two-photon chromophore.

In collaboration with **Marder, Ober, Clark, and Bunning** (AFRL/MLPJ), we have explored the use of two-photon microlithography for fabricating liquid-crystal-filled gratings (LCFGs). LCFGs may be useful in several optical applications, including electro-optic switching, free-space optical interconnects, and anti-jamming. Single layer grating structures (Fig. 10) were fabricated on ITO coated substrates treated with LC alignment layers. The structures were then packaged into cells and back-filled with 5CB and 7CB/5CB (4:1) mixtures. The alignment layers survive the microfabrication procedure such that the LC spontaneously forms a monodomain.

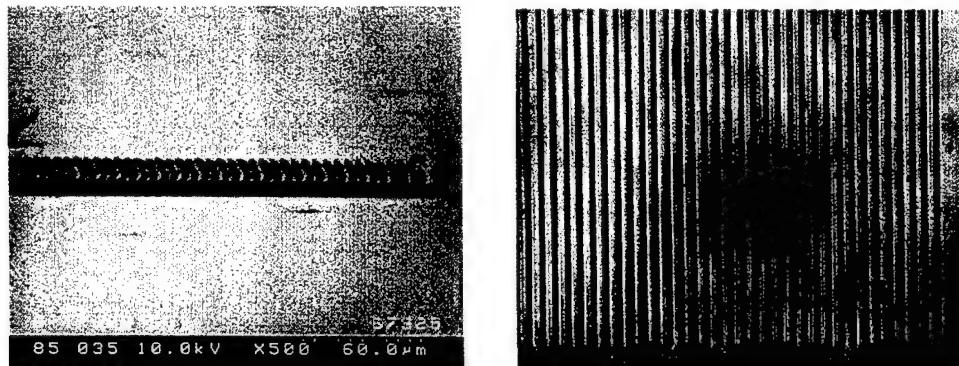


Figure 10. Left: Scanning electron micrograph of a single-layer 5-μm period grating. Right: Transmission image of the grating.

The diffraction and switching characteristics of the devices were examined. Fig. 11 shows the diffraction pattern obtained using a HeNe laser beam. The intensity of the 0th- and 1st-diffracted orders were monitored as a function of an applied 1kHz AC electric field (Fig. 11). The applied field poles the LC and results in a decrease in the diffraction strength with an associated increase in the 0th-order intensity.

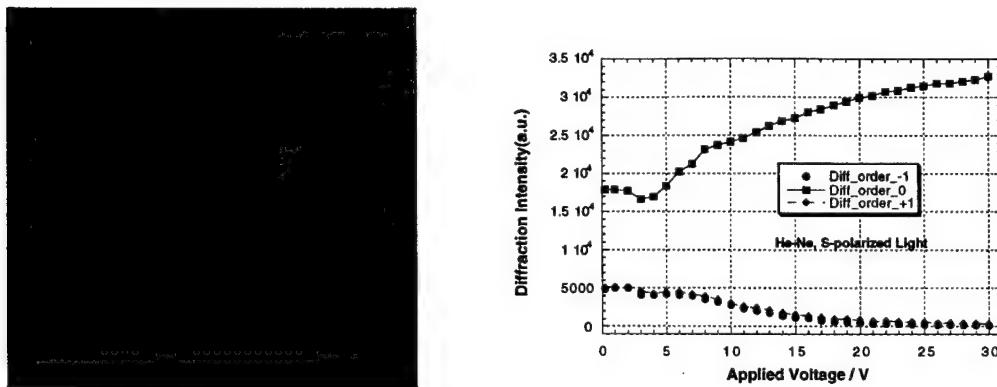


Figure 11. Left: Diffraction of a HeNe laser beam by a LC-backfilled single-layer grating showing the 0th (center) and  $\pm 1$  diffracted orders. Right: 0th- and 1st-order diffracted intensity versus applied AC field (1kHz).

This work has shown that we have the tools and the materials for fabricating LC-filled switchable grating structures. 3D structures have also been fabricated back-filled with LC materials. We plan to study the optical characteristics of these 3D structures and determine if switchable diffractive devices can be made. There are possible applications of this approach for 3-5  $\mu\text{m}$  beam steering. Grating structures and cells being fabricated for characterization at AFRL.

The acrylate-based resin system used for fabricating the gratings suffers from shrinkage, which distorts the structure and alters the optical properties. To improve the grating structures, we investigated the use of positive-tone solid-state resists for microfabrication of gratings in collaboration with **Marder** and **Ober**. Marder and Perry have developed high-sensitivity two-photon photoacid generators that can be used for patterning acid-sensitive materials. Ober's group has developed a series of solid-state chemically amplified resists (described above) based on cleavable side-chain ester groups, that are insoluble in aqueous media but become soluble in aqueous base in the presence of acid. Together we have formulated two-photon-patternable resins based on the two-photon photoacid generator shown in Fig. 12 and the chemically amplified resist THPMA-MMA, shown in Fig. 13, which can be used for high-fidelity 3D microfabrication.

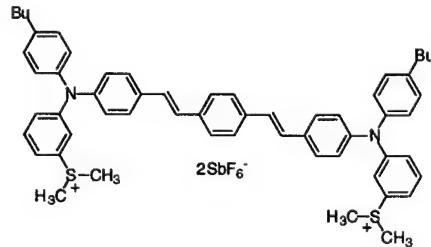


Figure 12. Two-photon photoacid generator BSB-S<sub>2</sub> based on a D- $\pi$ -D chromophore with pendant dimethylsulfonium groups.

Fig. 13A shows a target grating structure which was patterned in a positive resist formulation consisting of 2.5 wt.-% two-photon photoacid generator in THPMA-MMA. The structure

consists of 12 microchannels with a width of 4- $\mu\text{m}$ , lying 10  $\mu\text{m}$  below the surface of the film. Following exposure at 730 nm using 100-fs pulses, the structure was baked and developed to remove the exposed resin. The scanning electron micrograph (Fig. 13B) shows that the openings of the channels lie below the film surface and are open to the larger rectangular cavities, that extend to the film surface at either end. The two-photon fluorescence images (Fig. 13, C to F), taken after removing the exposed material, reveal that the channels are open and make a continuous connection between the cavities. We have also shown that these channels can be back-filled with liquids, including liquid crystals. This demonstration illustrates that this positive-tone resist material system can be used to pattern complex 3D structures. These results have recently been accepted for publication in *Science*. We are currently exploring the use of this material system for fabricating LC-filled gratings and more complicated switchable microoptical structures.

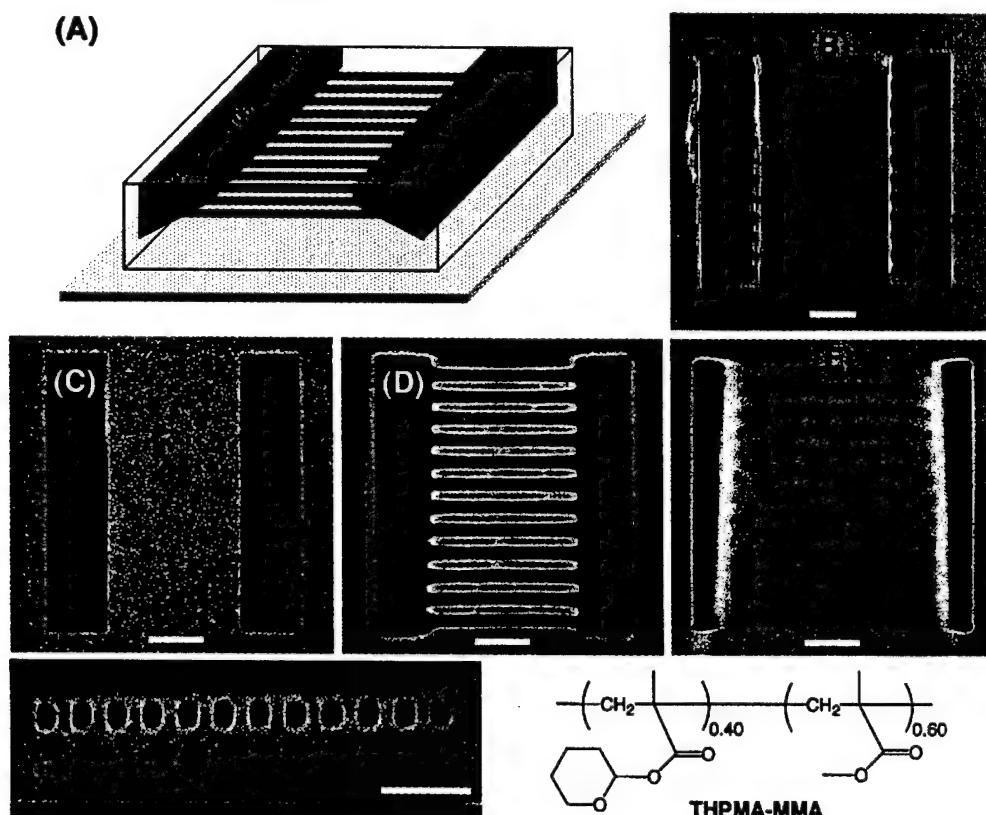
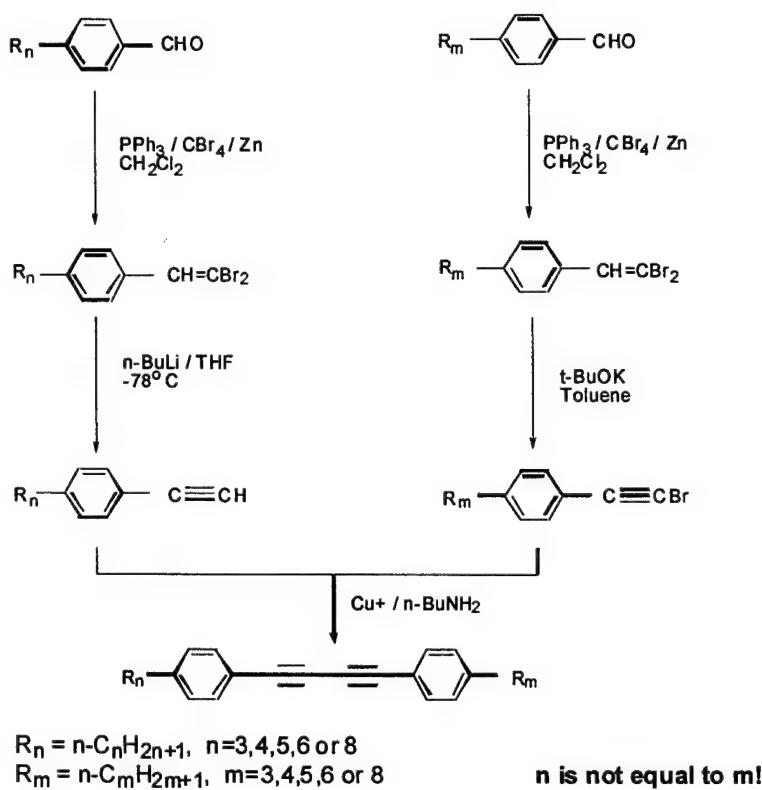


Figure 13. 3D grating structure fabricated by two-photon-exposure of **BSB-S<sub>2</sub>** in THPMA-MMA. (A) Target structure consisting of two rectangular cavities (width: 100  $\mu\text{m}$ , length: 20  $\mu\text{m}$ , depth: 20  $\mu\text{m}$ ) with a sloped side-wall, that are connected by 12 microchannels (length: 50  $\mu\text{m}$ ; 4- $\mu\text{m}$  by 4- $\mu\text{m}$  cross-section) lying 10  $\mu\text{m}$  below the surface and spaced apart by 8  $\mu\text{m}$  (center-to-center). (B) Scanning electron micrograph of the final structure, viewed normal to the substrate. (C to E) Two-photon-fluorescence images of the final structure (viewed normal to the substrate): (C) at the surface of the film; (D) 10  $\mu\text{m}$  below the surface; (E) 19  $\mu\text{m}$  below the surface. (F) Two-photon-fluorescence cross-sectional image of the buried channels. The scale bar in B to F corresponds to 20  $\mu\text{m}$ .

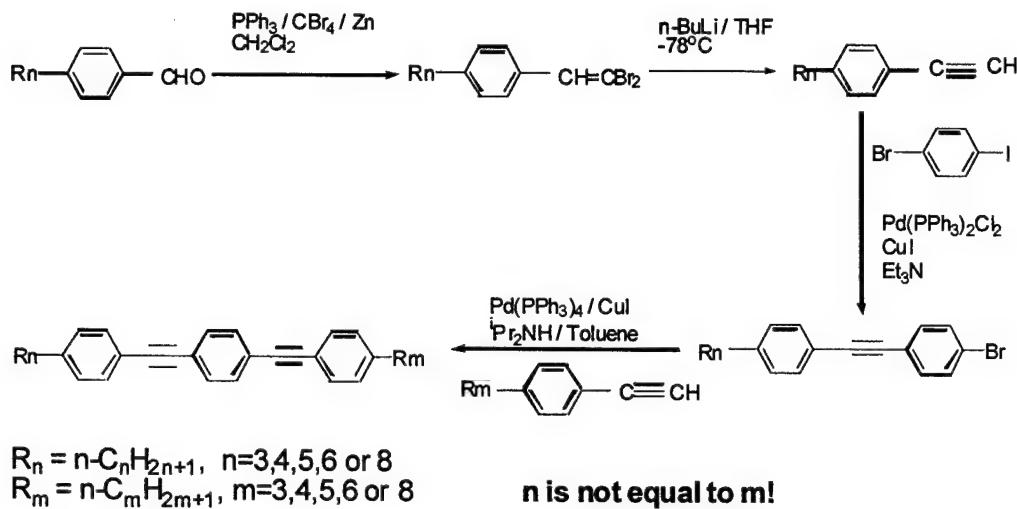
University of Washington, Seattle / University of Southern California

Dalton. We have synthesized a series of asymmetric diphenyl-diacetylene (PTTP) liquid crystals (Scheme 1), which provide a useful electro-optic medium for modulating infrared radiation and high-speed light shutters due to their high birefringence ( $\Delta n$ ) and relatively low viscosity. In particular, these materials have been utilized for device applications by Hughes Research Laboratories and by Raytheon. Clearly, there is a need to improve the birefringence of this class of nematic LC materials which led us to develop the PTPTP (Scheme 2) family of LC materials.

Scheme 1. Synthesis of PTTP.



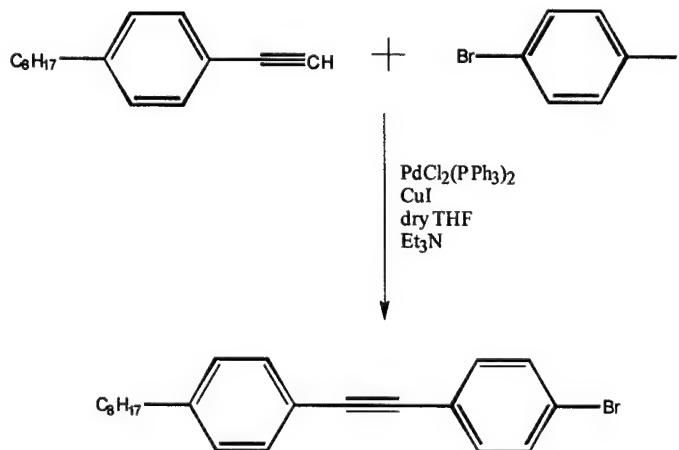
**Scheme 2. Synthesis of PTPTP**

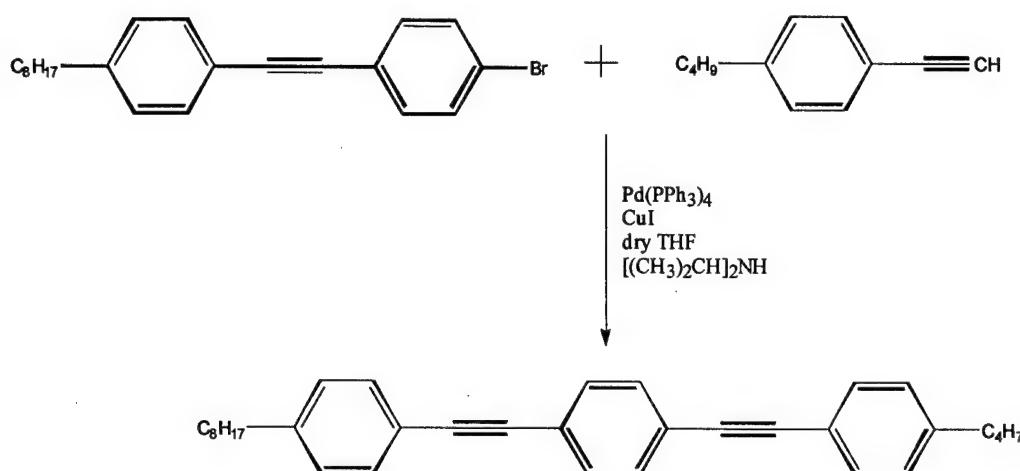


PTPTP incorporates one more phenyl group into the PTTP backbone, which increased the birefringence due to the conjugation length increase of the long axis. However this modification changed the physical properties of the liquid crystals as well, such as higher melting temperature. The asymmetric alkyl chains helped to lower the melting temperature significantly. Therefore, we synthesized the PTPTP homologues with different asymmetric alkyl terminal groups to explore the highest  $\Delta n$  that can be obtained while keeping melting temperature within an acceptable range. We started from PTPTP-48, -46 and -68, compounds which should give us birefringence around 0.46 in the visible region, compared to 0.40 for PTTP liquid crystal materials.

The synthesis of PTPTP-48 is shown below (scheme 3).

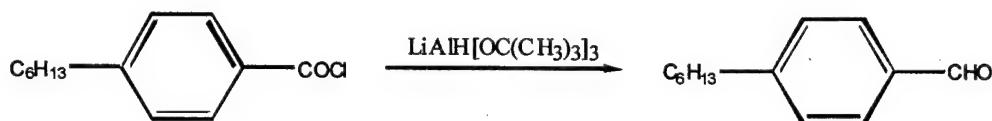
**Scheme 3:**





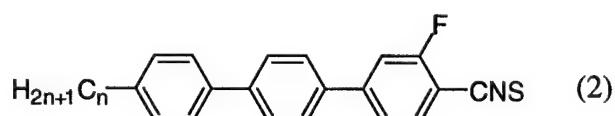
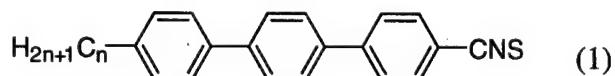
Because *p*-hexylbenzaldehyde or *p*-hexylbenzaldehyde-diethylacetal was not commercially available, we used reduction of acid chloride with lithium tri-*t*-butoxyaluminohydride to produce the *p*-hexylbenzaldehyde (Scheme 4). The following reactions from *p*-hexylbenzaldehyde to corresponding PTPTP are similar to above procedures.

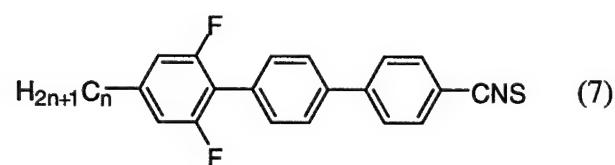
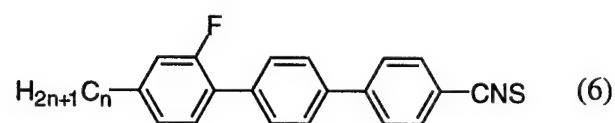
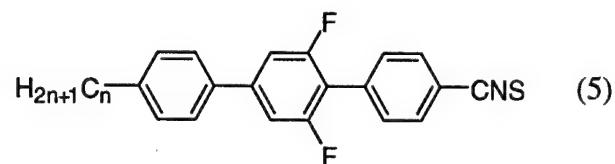
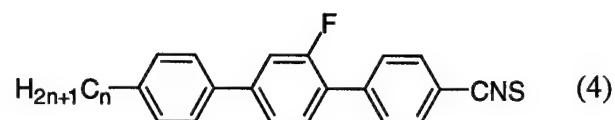
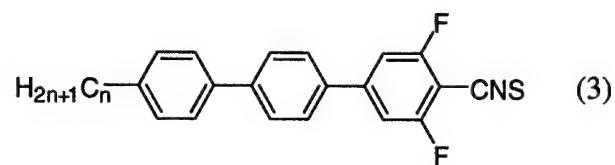
**Scheme 4:**



These materials were provided to **Dr. S. -T. Wu** of Hughes Research Laboratories. The synthesis of these materials is reported in: S. T. Wu, C. S. Hsu, K. F. Shyu, Y. Y. Chuang, H. B. Cheng, Z. Chai, G. Day, L. Guo and L. R. Dalton, "High Birefringence Bis-Tolane Liquid Crystals for Display Applications," *SID Tech. Digest*, **30**, 706-9 (1999).

Recent research has focused on preparing the following materials:





A patent has recently been filed by Hughes dealing with materials synthesized during the past two years.

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Julia A. Kornfield, California Institute of Technology

Robert Grubbs, California Institute of Technology

Noel Clark, University of Colorado

Christopher Ober, Cornell University

Ned Thomas, Massachusetts Institute of Technology

Wesley Burghardt, Northwestern University

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David Walba, University of Colorado  
Christopher Ober, Cornell University  
Peter Palffy-Muhoray, Kent State University  
Edwin L. Thomas, Massachusetts Institute of Technology  
Larry Dalton, University of Southern California  
Shin-Tson Wu, Hughes Research  
Bill Thurmes, Displaytech

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2. Dr. Qing Zhang, Postdoctoral Associate
3. Professor Joseph Perry, Research Member

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1. Dr. Seth Marder, Research Member (1996–1998)
2. Dr. Dan Dyer, Postdoctoral Scholar
3. Professor Girija Subramanian (Penn. State Univ., Hazelton), travel and supplies only
  
1. Professor Julia A. Kornfield, Faculty
2. Mr. Weijun Zhou, Graduate Student
3. Ms. Bhavna Hirani, Technician
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4. Ms. Lie Xiao, Graduate Student
7. Dr. Dan Dyer, Graduate Student
8. Li-Xing Wang, Graduate Student
  
1. Professor Noel A. Clark, Faculty
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6. Ms. Padma Gopalan, Graduate Student
7. Mr. Xuefa Li, Graduate Student

8. Mr. Mingqi Li, Graduate Student
9. Mr. Norman Chao, Graduate Student

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6. Haijun Yuan, Graduate Student
7. Dr. Miguel Camacho, Postdoctoral Fellow
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9. Feng Liu, Graduate Student
10. Conan Teng, Graduate Student
11. Shashi Guptha, Graduate Student

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6. Ms. Cecilia Calvo, Senior Secretary
7. Ms. Jean DeAngelis, Administrative Assistant
8. Ms. Joycelyn Plant, Undergraduate Student
9. Ms. Carolyn Philips, Undergraduate Student
10. Ion Bita, Graduate Student

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2. Mr. Lan Guo, Graduate Student
3. Mr. Fang Wang, Graduate Student
4. Mr. Albert Ren, Graduate Student
5. Dr. Zheng Chai, Postdoctoral Fellow
6. Dr. Gary Day, Postdoctoral Fellow
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4. Dr. Qing Zhang, Postdoctoral Scholar
5. Dr. Timothy Parker, Postdoctoral Scholar
  
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2. Dr. Jeff Ehrlich, Postdoctoral Scholar
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(The following graduate students received partial support)

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2. Feng Liu, Graduate Student
3. Conan Teng, Graduate Student
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## Publications

Z.-R. Chen, J. A. Kornfield, S. D. Smith, J. T. Grothaus and M. M. Satkowski, "Pathways to Macroscale Order in Nanostructured Block Copolymers," *Science* **277**, 1248 (1997).

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B. Temelkuran, E.L. Thomas, J.D. Joannopoulos and Y. Fink, "Low-loss IR Dielectric Material System for Broadband Dual Range Omnidirectional Reflectivity", *Optics Letters* **26**, 1370-1372 (2001).

P. Huang, L. Zhu, Q. Ge, R.P. Quirk and S.Z.D. Cheng, "Crystal Orientation Changes in Two-Dimensionally Confined Nano-cylinders in a Poly(ethylene oxide)-*b*-polystyrene/Polystyrene Blend", *Macromolecules* **34**, 6649-6657 (2001).

M.J. O'Rourke, D.-K. Ding, E.L. Thomas and V. Percec, "Morphologies and Energies of Néel Inversion Wall Defects in a Liquid Crystal Polyether," *Macromolecules* **34**, 6658-6669 (2001).

W.G. Jang and N.A. Clark, "Time-resolved infrared spectroscopy of nematic liquid crystal electro-optic switching," *Physical Review E* **63**, 031707 (2001).

Y.V. Pereverev, O.V. Prezhdo and L.R. Dalton, "Mean Field Theory of Accentric Order of Dipolar Chromophores in Polymeric Electro-Optic materials. Chromophores with Displaced Dipoles," *Chem. Phys. Lett.* **340**, 328-335 (2001).

K Takada, P. Gopalan, C.K. Ober and H.D. Abruña, "Synthesis, Characterization and Redox Reactivity of Novel Quinone Containing Polymers," *Chem. Materials* **13**(9), 2928-2932 (2001).

P. Gopalan, L. Andruzzi, X. Li, and C.K. Ober, "Fluorinated Mesogen Jacketed Liquid Crystalline Polymers as Low Surface Energy Materials: Design, Synthesis and Characterization," *Macromol. Chem. Phys.*, submitted.

P. Palffy-Muhoray, T. Kosa and W. E, "Brownian motors in the photoalignment of liquid crystals," *Appl. Phys. A-Mater.* **75**, 294 (2002).

## Presentations

Janelle Gunther and Edwin L. Thomas, "Origins of Defect Texture in Liquid Crystal Polymers," American Physical Society Meeting, Kansas City, March 1997.

V. M. Ugaz and W. R. Burghardt, "X-ray Scattering Study of Molecular Orientation in a Thermotropic LCP under Shear," Paper I'30.01, American Physical Society National Meeting, Kansas City, March, 1997. *APS Bulletin*, **42**(1) 410 (1997).

C.K. Ober, "Microphase Stabilized Ferroelectric Liquid Crystal (MSFLC): Bistable Switching of FLC-Coil Diblock Copolymers," American Physical Society Meeting, Kansas City, March 1997.

C.K. Ober, "Self-Assembly of Fluorinated LC Block Copolymers with a Stable Low Energy Surface," American Chemical Society, San Francisco, April 1997.

C. Ober, "Microphase Stabilized Ferroelectric Liquid Crystal (MSFLC): Bistable Switching of FLC-Coil Diblock Copolymers," American Physical Society Meeting, Kansas City, March 1997.

C. Ober, "Self-Assembly of Fluorinated LC Block Copolymers with a Stable Low Energy Surface," American Physical Society Meeting, Kansas City, March 1997.

C. Ober, "Microphase Stabilized Ferroelectric Liquid Crystal (MSFLC): Bistable Switching of FLC-Coil Diblock Copolymers," American Chemical Society, San Francisco, April 1997.

C. Ober, "Self-Assembly of Fluorinated LC Block Copolymers with a Stable Low Energy Surface," American Chemical Society, San Francisco, April 1997.

T. Kosa, P. Palffy-Muhoray, "Kinetics of Photoinduced Orientation of Azo-dyes in alignment layers," QELS'97, Baltimore, May, 1997.

T. Kosa, P. Palffy-Muhoray, "Kinetics of photoinduced orientation," T. Kosa (invited) Topical Meeting on Optics of Liquid Crystals, Heppenheim, Germany, Sept. 1997.

P. Palffy-Muhoray, "Angular Momentum Balance in the Janossy Effect," Topical Meeting on Optics of Liquid Crystals, Heppenheim, Germany, Sept. 1997.

A. Reyes and P. Palffy-Muhoray, "Nonlinear Schrodinger Equation in Nematics," Topical Meeting on Optics of Liquid Crystals, Heppenheim, Germany, Sept. 1997.

T. Kosa, P. Palffy-Muhoray, "Kinetics of Photoinduced Orientation of Azo-dyes in alignment layers," Topical Meeting on Organic Thin Films for Photonic Applications Long Beach, CA Oct. 1997.

D. Walba, "Ferroelectric Liquid Crystals for Nonlinear Optics," Invited Talk, 1997 European Conference on Liquid Crystals, Zakopane, Poland, March 1997.

D. Walba, "Ferroelectric Liquid Crystals," Invited Talk, 1997 Gordon Research Conference on Liquid Crystals, Tilton, NH, June 1997.

P. Palffy-Muhoray, (plenary), "Nonlinear Optics of Liquid Crystals", XX Condensed Matter Meeting of the Brazilian Physical Society, Caxambu, (June 12, 1997).

T. Kosa, P. Palffy-Muhoray, "Kinetics of Photoinduced Orientation of Azo-dyes in alignment layers", QELS'97, Baltimore, (May 1997).

J. Perry, "Nonlinear Spectroscopy and Applications of Two-Photon Absorbing Molecules", American Physical Society Meeting, Kansas City, (March 1997).

J. E. Ehrlich, X.-L. Wu, I.-Y. S. Lee, A. A. Heikal, Z.-Y. Hu, S. R. Marder, and J. W. Perry, "Two-Photon Absorbing Organic Chromophores for Optical Limiting", Mat. Res. Soc. Meeting., San Francisco, (March 1997).

V. M. Ugaz and W. R. Burghardt, "X-ray Scattering Study of Molecular Orientation in a Model Thermotropic Liquid Crystalline Polymer During Steady and Transient Shear Flows," Poster PO15, Society of Rheology National Meeting, Columbus, October, 1997.

V. M. Ugaz and W. R. Burghardt, "In Situ X-ray Scattering Studies of Model Thermotropic Liquid Crystalline Polymers under Shear," Paper 178g, AIChE National Meeting, Los Angeles, November 1997.

V. M. Ugaz and W. R. Burghardt, "X-ray Scattering Investigation of Molecular Orientation During Shear Flow in Model Thermotropic Liquid Crystalline Polymers," Paper I11 4, American Physical Society National Meeting, Los Angeles, March, 1998. *APS Bulletin*, **43**(1) 274 (1998).

D. K. Cinader, Jr. and W. R. Burghardt, "X-ray Scattering Measurements of Molecular Orientation in Channel Flows of a Thermotropic Liquid Crystalline Polymer," Paper S8 1, American Physical Society National Meeting, Los Angeles, March, 1998. *APS Bulletin*, **43**(1) 687 (1998).

W. R. Burghardt, H. Siebert & C. Schmidt, "Rheo-NMR of Lyotropic and Thermotropic Main Chain LCPs," Poster O38 133, American Physical Society National Meeting, Los Angeles, March, 1998. *APS Bulletin*, **43**(1) 597 (1998).

C. Osuji, E. L. Thomas, G. Mao and C. K. Ober, "Structure and Properties of Smectic Mesophases Confined to Block Copolymer Microdomains" American Physical Society Meeting, Kansas City, March 1997

C. K. Ober, University of Wuppertal, Wuppertal, Germany, July 1, 1998. "Tailoring Polymer Thin Film Properties By Balancing Selected Molecular Interactions"

C. K. Ober, University of Marburg, Marburg, Germany, June 30, 1998. "Tailoring Polymer Thin Film Properties By Using Both Self- And Directed-Assembly"

C. K. Ober, Unifying Principles for Engineering Soft Materials, Risø National laboratory, Denmark, June 22 - 25, 1998. "Competing Molecular Interactions as a Means for Engineering Soft Materials", invited talk.

C. K. Ober, Polymer (East) Gordon Research Conference, New England College, Henniker, NH, June 14-19, 1998. "Adjusting Macromolecular Structure Using Competing Molecular Interactions", invited talk.

C. K. Ober and S. Pragliola, American Chemical Society Meeting, Dallas, TX, Mar. 29 - Apr. 2, 1998. "The Design Of Specialty Monomers For Advanced Applications", invited talk

C. K. Ober, University of Virginia, Charlottesville, VA, March 2, 1998. "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation", invited talk.

Z.-R. Chen, A. M. Issaian, J. A. Kornfield, S. D. Smith, J. T. Grothaus, M. M. Satkowski, "Pathways to Macroscale Order in Nanostructured Block Copolymers," American Physical Society, Los Angeles, March 1998.

Y. L. Chen, Z.-R. Chen, A. M. Issaian, J. A. Kornfield, S. D. Smith, A. Ashraf, "Alignment Behavior of Lamellar ABC Triblock Copolymers and Blends," American Physical Society, Los Angeles, March 1998.

J. A. Kornfield, Z.-R. Chen, A. M. Issaian, Y. L. Chen, S. D. Smith, A. Ashraf, J. T. Grothaus, M. M. Satkowski, "Defect Dynamics of Three-Nanophase-Separated ABC TriblockCopolymers," American Physical Society, Los Angeles, March 1998.

W. Zhou, J. A. Kornfield, "Effect of Phase Transition on the Rheology of Model Thermotropic Liquid Crystalline Polymers," American Physical Society, Los Angeles, March 1998.

P. Palffy-Muhoray, "Brownian Motors in the Photoalignment of Liquid Crystals", Eringen Medal Symposium for P.G. de Gennes, 35<sup>th</sup> Annual Technical Meeting of the Society of Engineering Science, Washington State University, Pullman, Sept. 27, 1998.

P. Palffy-Muhoray, "Orientational Ratchets and Molecular Motors in the Photoalignment of Liquid Crystals", 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, July, 1998.

P. Palffy-Muhoray, "Ratchets, Molecular Motors and the Photoalignment of Liquid Crystals", FENOMECH, UNAM, Mexico City, June 1, 1998.

P. Palffy-Muhoray, "Ratchets, Molecular Motors and the Photoalignment of Liquid Crystals", Liquid Crystal Institute, Kent State University, Feb. 25, 1998.

P. Palffy-Muhoray, "Nonlinear Optics of Liquid Crystals", University of Akron, Oct. 3, 1997.

P. Palffy-Muhoray, "Wavelength Selection in Dissipative Systems Slowly Driven from Equilibrium", Patterns, Non-Linear Dynamics and Stochastic Behaviour in Spatially Extended Complex Systems, Budapest, Oct. 23-28, 1997.

R. Ennis, P. Palffy-Muhoray and W. E, "Numerical Studies of Phase Separation in Liquid Crystalline Binary Mixtures", 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, July 19-24, 1998.

H. Yuan and P. Palffy-Muhoray, "Waveguide Based Liquid Crystal Display", 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, July 19-24, 1998.

R. Ennis, L. Kondic, M.J. Shelley and P. Palffy-Muhoray, "Viscous Fingering in Shear Thinning Fluids", 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, July 19-24, 1998.

S.G. Lukishova, T. Kosa, B. Taheri and P. Palffy-Muhoray, "Nanosecond Z-Scan Measurements of Optical Nonlinearities in 5CB and CB15", 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, July 19-24, 1998.

H. Yuan, W. E, T. Kosa and P. Palffy-Muhoray, "Analytic 4 x 4 Propagation Matrices for Homogeneous Media", 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, July 19-24, 1998.

P. Palffy-Muhoray and W. E, "Formation and Dynamics of Filaments at the Isotropic-Smectic A Transition", 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, July 19-24, 1998.

T. Kosa and P. Palffy-Muhoray, "Temperature Dependence of Optical Orientation of Chromophores in LC Alignment Layers", 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, July 19-24, 1998.

P. Palffy-Muhoray and W. E, "Transport in a Driven Ratchet", March Meeting of the APS, Los Angeles, March 16-20, 1998.

H. Yuan, W. E, T. Kosa and P. Palffy-Muhoray, "New 4 x 4 Matrix Method for Light Propagation in Liquid Crystals", March Meeting of the APS, Los Angeles, March 16-20, 1998.

T. Kosa and P. Palffy-Muhoray, "Kinetics of Photoinduced Orientation of Azo-dyes in Alignment Layers", March Meeting of the APS, Los Angeles, March 16-20, 1998.

M. Shelley, P. Fast, L. Kondic, R. Ennis and P. Palffy-Muhoray, "Pattern Formation in Non-Newtonian Hele-Shaw Flow", March Meeting of the APS, Los Angeles, March 16-20, 1998.

S. T. Wu, Molecular engineering of liquid crystals for display application (Invited Lecture) Physics Department, University of Southern California, (Oct.27, 1997).

S. T. Wu, "Reflective TFT TN displays" Invited talk at KSU ALCOM reflective display symposium, (Dec.11-12, 1997).

S. T. Wu "Overview on reflective liquid crystal displays using one polarizer" Invited talk at Photonics Taiwan Conference, Taipei, Taiwan (July 9-11, 1998).

S. T. Wu, "Reflective liquid crystal displays" Invited talk at Siliscape Inc., San Jose, California (August 7, 1998).

L. Dalton - 1998 IEEE/LEOS Summer Topical Meeting, Organic Optics and Optoelectronics.

L. Dalton - First International Workshop on Optical Power Limiting, Cannes, France, 1998.

L. Dalton - The International Society of Optical Engineering 43rd Annual Meeting, San Diego, 1998.

L. Dalton - University of California at Los Angeles and the Max-Planck-Institut fur Polymerforschung (Mainz FRG).

L. Dalton - Department of Chemistry and Biochemistry, University of California at Los Angeles.

L. Dalton - Department of Chemistry, University of California at Santa Barbara.

B. W. Lee and N. A. Clark, "Patterned Amorphous Self Assembled Monolayers for Liquid Crystal Displays," 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, France, 1998.

S. Bardon, D. Coleman, N.A. Clark, D.M. Walba, X.H. Chen, and M.D. Wand, "Director Orientation of the Surface in "Thresholdless" Antiferroelectric Surface Stabilized FLC Cells," 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, France, 1998.

P. Palffy-Muhoray, "Orientational Ratchets and Molecular Motors in the Photoalignment of Liquid Crystals", 17<sup>th</sup> International Liquid Crystal Conference, Strasbourg, (July 21, 1998).

P. Palffy-Muhoray, "Ratchets, Molecular Motors and the Photoalignment of Liquid Crystals", FENOMEC, UNAM, Mexico City, (June 1, 1998).

P. Palffy-Muhoray, "Ratchets, Molecular Motors and the Photoalignment of Liquid Crystals", Liquid Crystal Institute, Kent State University, Feb. 25, 1998

P. Palffy-Muhoray, "Nonlinear Optics of Liquid Crystals", University of Akron (Oct. 3, 1997).

S. Barlow, B.H. Cumpston, G. Duerksen, J.-Y. Fu, J.E. Ehrlich, A.A. Heikal, T. Kosa, S. Kuebler, I.-Y. S. Lee, S. Lukishova, K. Mansour, S.R. Marder, D. McCord-Maughon, P. Palffy-Muhoray, J.W. Perry, H. Röckel, M. Rumi, G. Subramaniam, B. Taheri, S. Thayumanvan, X.-L. Wu, "Two-Photon Absorbing Materials for Optical Power Limiting and Imaging," "Nonlinear Optical Liquids for Power Limiting and Imaging," SPIE's International Symposium on Optical Science, Engineering & Instrumentation; San Diego, CA (July 19-24, 1998).

S. Barlow, B. H. Cumpston, G. Duerksen, J.-Y. Fu, J.E. Ehrlich, A. A. Heikal, T. Kosa, S. Kuebler, I.-Y. S. Lee, S. Lukishova, K. Mansour, S.R. Marder, D. McCord-Maughon, P. Palffy-Muhoray, J.W. Perry, H. Röckel, M. Rumi, G. Subramaniam, B. Taheri, S. Thayumanvan, X.-L. Wu, "Two-Photon Absorbing Materials for Optical Limiting," First International Workshop on Optical Power Limiting, Cannes, France (June 28-July 1, 1998).

J. Perry, "Structure-Property Relationships and Applications of Two-Photon Absorbing Molecules," Liquid Crystal Institute, Kent State University (June 10, 1998).

C. K. Ober, "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation," University of Massachusetts, October, 1998.

C. K. Ober, "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation," MIT, November, 1998.

C. K. Ober, "Balancing Liquid Crystallinity with Microphase Separation in Block Copolymers: Does the Tail Wag the Dog?", University of Illinois Champaign, February, 1999.

C. K. Ober, "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation," University of Southern Illinois, April, 1999.

C. K. Ober, "Balancing Liquid Crystallinity with Microphase Separation in Block Copolymers," Princeton University, April, 1999.

C. K. Ober, "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation," Kyoto University, June, 1999.

C. K. Ober, "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation," Naval Research Laboratories, June, 1999.

C. K. Ober, P. Gopalan, S. Pragliola, P. T. Mather, H. G. Jeon, "Mesogen-Jacketed Liquid Crystalline Polymers Via Stable Free Radical Polymerization", American Chemical Society Meeting, New Orleans, LA, August, 1999.

E. L. Thomas and Y. Zhang, "Disclination Dynamics in LCPs", University of Ulm, Germany October, 1998.

E. L. Thomas, "Structural Studies of LCPs," WPAFB, Dayton Ohio, November, 1998.

E.L. Thomas, C. Osuji, Y. Zhang, C. Philips, G.Mao and C.K. Ober, "Microstructured Liquid Crystalline Polymers," Materials Research Society, December, 1998.

E. L. Thomas, Nanostructure Polymeric Systems," NRC Nanostructure Study, Washington DC, March, 1999.

C. Osuji, E.L. Thomas, C. K. Ober, "Orientation of LCP Block Copolymers," American Physical Society, March 1999.

W. R. Burghardt, "X-ray scattering studies of LCPs under flow," Rheology Research Center, University of Wisconsin, February 12, 1999.

W. R. Burghardt, "X-ray scattering studies of molecular orientation in main-chain thermotropic liquid crystalline polymers under shear," Plenary Lecture, Eurorheo99: Rheology, Rheo-physics and Flow-Induced Structures of Liquid Crystal Polymers, Surfactants and Block Copolymers, Sophia-Antipolis, France, May 1999.

D. K. Cinader, Jr. and W. R. Burghardt, "In Situ X-ray Scattering Measurements of Molecular Orientation in Channel Flows of Thermotropic Liquid Crystalline Polymers," ACS National Meeting, Boston, August 1998. *Proc. ACS Div. PMSE*, **79**, 361 (1998).

V. M. Ugaz and W. R. Burghardt, "In Situ X-ray Scattering Investigation of the Influence of Shear and Thermal Histories on Molecular Alignment in a Model Thermotropic Liquid Crystalline Polymer," ACS National Meeting, Boston, August 1998. *Proc. ACS Div. PMSE*, **79**, 369 (1998).

W. Zhou, J. A. Kornfield, V. M. Ugaz and W. R. Burghardt, "Dynamics and Alignment Behavior of a Thermotropic Liquid Crystalline Polymer," Paper CF2, Society of Rheology National Meeting, Monterey CA, October 1998.

D. K. Cinader, Jr. and W. R. Burghardt, "X-ray Scattering Measurements of Molecular Orientation in Channel Flows of a Thermotropic Liquid Crystalline Polymer," Paper CF6, Society of Rheology National Meeting, Monterey, CA, October 1998.

J. A. Kornfield, W. Zhou, W. R. Burghardt and V. M. Ugaz, "X-ray Scattering Investigation of the Interplay Between Molecular Orientation and Rheology in a Model Thermotropic Liquid Crystalline Polymer," paper 127i, AIChE National Meeting, Miami Beach, November 1998.

J. A. Kornfield, W. Zhou, W. R. Burghardt "Classification of Flow-aligning vs Director Tumbling Character of a Model Thermotropic LCP," paper 127j, AIChE National Meeting, Miami Beach, November 1998.

W. Zhou, J. A. Kornfield and W. R. Burghardt, "Visualization of Director Evolution under Weak Shear Flow for a Model Thermotropic Liquid Crystalline Polymer," Paper XC12.05, American Physical Society National Meeting, Atlanta, March 1999. *APS Bulletin*, **44**(1) 1758 (1999).

D. K. Cinader, Jr. and W. R. Burghardt, "In Situ X-Ray Scattering Measurements of Molecular Orientation in Channel Flows of Thermotropic Liquid Crystalline Polymers," Paper XC12.06, American Physical Society National Meeting, Atlanta, March 1999. *APS Bulletin*, **44**(1) 1758 (1999).

W. Zhou, J. A. Kornfield, V. M. Ugaz and W. R. Burghardt, "Dynamics and Alignment Behavior of a Thermotropic Main-Chain Liquid Crystalline Polymer," Paper D4.10, Materials Research Society Spring Meeting, San Francisco, April, 1999.

W. Zhou, "Effect of Molecular Weight and Temperature on the Rheological Properties of Thermotropic LCP," Society of Rheology, Columbus (October, 1997).

W. Zhou, "Effect of Phase Transitions on the Dynamics and Flow Alignment Behavior of a Model Thermotropic LCP," American Physical Society, Los Angeles (March, 1998).

W. Zhou, "Classification of Flow-aligning vs. Tumbling for Thermotropic LCPs," American Institute of Chemical Engineering, Miami (November, 1998).

W. Zhou, "Interplay between Microstructure, Dynamics and Alignment in a Thermotropic LCP," Society of Rheology, Monterey, CA (October, 1998).

W. Zhou, "Direct Visualization of Director Orientation under Weak Transient Shear Flow", American Physical Society, Atlanta, (March, 1999).

J. A. Kornfield, "Dynamics and Shear Orientation Behavior of a Model Thermotropic LCP", Materials Research Society, San Francisco (April, 1999).

J. A. Kornfield, "Orientational Flipping and Flow Alignment of a Model Thermotropic Liquid-crystalline Polymer," American Chemical Society National Meeting, New Orleans (August, 1999).

D. Walba, Invited Talk, Fifth International Display Workshop, Kobe, Japan, "On the Phase Formerly Known as Thresholdless Antiferroelectric," December 8, 1998.

D. Walba, Queen's University, Kingston, Ontario, Canada, "Supermolecular Stereochemistry in Liquid Crystals," March 3, 1999.

D. Walba, Naval Research Laboratory, Washington, D.C., "Design and Synthesis of a Ferroelectric Smectic Liquid Crystal Composed of Racemic Molecules," March 8, 1999.

D. Walba, R.E. Ireland 70<sup>th</sup> Birthday Symposium, Anaheim, California, "Supermolecular Stereochemistry," March 26, 1999.

D. Walba, MRS National Meeting, San Francisco, CA, "Chiral Liquid Crystals from Achiral and Racemic Molecules" April 5, 1999.

D. Walba, SPIE Symposium on Liquid Crystals III, Denver, Colorado, "Ferroelectric smectic liquid crystal in the bent-core family showing selectable V-shaped or bistable ferroelectric switching in the same cells," July 21, 1999.

D. Walba, Invited Lecture for 11th International Symposium on Chiral Discrimination, Chicago, Illinois, "Chiral liquid crystals from achiral molecules: A liquid conglomerate," July 26, 1999.

D. Walba, Invited lecture for the International Symposium on Anisotropic Organic Materials, held in conjunction with the 218<sup>th</sup> National Meeting of the American Chemical Society, "Supermolecular Stereocontrol in Chiral Smectic LCs using Layer Interface Clinicity," August 23, 1999.

"Directed Design of an Achiral Antiferroelectric Phase" D.M. Walba, E. Korblova, R. Shao J. MacLennan, D.R. Link, N.A. Clark, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Spontaneous Formation of a Chiral Fluid Phase from Achiral Molecules," N.A. Clark, D.R. Link, G. Natale, R. Shao, J.E. MacLennan, E. Korblova and D.M. Walba, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Evidence for a Double-well Interlayer Orientational Potential in the Smectic Phase," D.R. Link, G. Natale, J.E. MacLennan, N.A. Clark, M. Walsh, S.S. Keast and M.E. Neubert, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Study of Thin Smectic Liquid Crystal Films by Atomic Force Microscopy," S. Bardon, B.W. Lee and N.A. Clark, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Microscopic Organization of the Smectic Phase," M.A. Glaser, Y. Lansac, T. Weider and N.A. Clark, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Photo-induced Nanophase Segregation in a Smectic Liquid Crystal," Y. Lansac, M.A. Glaser and N.A. Clark, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Dynamic Optical Spectrometry of Switching Ferroelectric Liquid Crystals," J. E. MacLennan, M.-N. Gong and N.A. Clark, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Anticlinic Tilted Surfaces on Freely Suspended Smectic A Films," D.R. Link, G. Natale, J.E. MacLennan, N.A. Clark, M. Walsh, S.S. Keast and M.E. Neubert, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Ring Pattern Dynamics in Freely Suspended Films," D.R. Link, G. Natale, L. Radzhivsky, J.E. MacLennan, N.A. Clark, M. Walsh, S.S. Keast and M.E. Neubert, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Freely Suspended Films of Banana-like Mesogens," D.R. Link, G. Natale, E. Korblova, J.E. MacLennan, N.A. Clark and D.M. Walba, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Patterned Amorphous Self-assembled Monolayers as Alignment Layers for Liquid Crystal Displays," B.W. Lee and N.A. Clark, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"Director Orientation of the Surface in "Thresholdless" Antiferroelectric Surface Stabilized FLC Cells," S. Bardon, D. Coleman, N.A. Clark, D. Walba, X.H. Chen and M. Wand, 17th International Liquid Crystal Conference, Strasbourg, France, July 1998.

"V-Shaped Switching in Ferroelectric Liquid Crystals," J.E. MacLennan, P. Rudquist, R. Shao, D.R. Link, D.M. Walba, N.A. Clark, and S.T. Lagerwall, Presented at the Conference on Liquid Crystals, Society of Photo-optical Instrumentation Engineers Annual Meeting, Denver, CO (1999).

J. A. Kornfield, "The Dynamics of Side-Group Liquid Crystalline Polymers," Materials Research Society Spring Meeting, San Francisco (April 1999).

J. A. Kornfield, "Orientational Coupling between Side-Group Liquid-Crystalline Polymers and Nematic Solvents," Materials Research Society Fall Meeting (December 1998).

J. A. Kornfield, "Dynamics of Side-Group Liquid Crystalline Polymers," American Chemical Society National Meeting (August 1998).

J. A. Kornfield, "Nematic Solutions of Large Molecular Weight Side-group Liquid-crystal Polymers," American Chemical Society National Meeting, New Orleans (August 1999).

Ober, Nitto Denko, Kyoto, Japan, June 30, 1999. "Fundamental Studies of Polymer Architecture Advanced Lithography", *invited talk*

C. Ober, Kyoto University, Kyoto, Japan, June 30, 1999. "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation", *invited talk*.

C. Ober, Naval Research Laboratories, Arlington, VA, June 7, 1999. "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation", *invited talk*.

C. Ober, Princeton University, Princeton, NJ, April 21, 1999. "Balancing Liquid Crystallinity with Microphase Separation in Block Copolymers: Does the Tail Wag the Dog?", *invited talk*.

C. Ober, University of Southern Illinois, Carbondale, IL, April 2, 1999. "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation", *invited talk*.

C. Ober, UIUC, Champaign-Urbana, IL, Feb. 22, 1999. "Balancing Liquid Crystallinity with Microphase Separation in Block Copolymers: Does the Tail Wag the Dog?", *invited talk*.

C. Ober, MIT, Cambridge, MA, Nov. 6, 1998. "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation", *invited talk*.

C. Ober, UMASS, Amherst, MA, Oct. 16, 1998. "Creating Ordered Materials by the Interplay of Liquid Crystallinity and Microphase Separation", *invited talk*.

C. Ober, Polycondensation '98, Annapolis Royal, VA, Sept. 29, 1998. "Recent Developments in LC Thermosets", *invited talk*.

L. Dalton, PHY/COMP Co-Sponsored Symposium New Orleans ACS Meeting (Invited) "A Theoretical Analysis of the Competition of Intermolecular Electrostatic Interactions and Applied Electric Fields in Defining Phases of Matter" Aug. 25, 1999.

L. Dalton, Poznan, Poland NATO ACI Workshop (Invited) "Control of Optical Properties Using Various Nanostructured Materials: Dendrimers, Phase-Separating Block Copolymers, and Polymer Microspheres," June 24, 1999.

P. Palffy-Muhoray, "Photoalignment of Liquid Crystals", Gordon Conference on Liquid Crystals, Tilton, NH, June 6-11, 1999

P. Palffy-Muhoray, "Light Propagation in Chiral Materials", ALCOM Symposium on Chirality, Cuyahoga Falls, Feb. 19, 1999

P. Palffy-Muhoray, "Ratchets, Brownian Motors and the Photoalignment of Liquid Crystals", Queen's College, CUNY, New York, Dec. 17, 1998.

P. Palffy-Muhoray, "Molecular Motors in the Photoalignment of Liquid Crystals", Simon Fraser University, Burnaby, Oct. 1, 1998

"Brownian Motors in the Photoalignment of Liquid Crystals", Eringen Medal Symposium for P.G. de Gennes, 35<sup>th</sup> Annual Technical Meeting of the Society of Engineering Science, Washington State University, Pullman, Sept 27, 1998

"Two-Photon Absorbing Materials for Optical Power Limiting and Imaging," S. Barlow, B.H. Cumpston, G. Duerksen, J.-Y. Fu, J.E. Ehrlich, A.A. Heikal, T. Kosa, S. Kuebler, I.-Y. S. Lee, S. Lukishova, K. Mansour, S.R. Marder, D. McCord-Maughon, P. Palffy-Muhoray, J.W. Perry, H. Röckel, M. Rumi, G. Subramaniam, B. Taheri, S. Thayumanvan, X.-L. Wu, in "Nonlinear Optical Liquids for Power Limiting and Imaging" SPIE's International Symposium on Optical Science, Engineering, and Instrumentation; San Diego, CA, (July 19-24, 1998).

"Two-Photon Absorbing Materials for Optical Limiting," S. Barlow, B. H. Cumpston, G. Duerksen, J.-Y. Fu, J.E. Ehrlich, A. A. Heikal, T. Kosa, S. Kuebler, I.-Y. S. Lee, S. Lukishova, K. Mansour, S.R. Marder, D. McCord-Maughon, P. Palffy-Muhoray, J.W. Perry, H. Röckel, M. Rumi, G. Subramaniam, B. Taheri, S. Thayumanvan, X.-L. Wu, First International Workshop on Optical Power Limiting, Cannes, France, (June 28-July 1, 1998).

"Structure/Property Relationships and Applications of Two-Photon Absorbing Molecules," M. Rumi, J. E. Ehrlich, B. Cumpston, S. Kuebler, A. A. Heikal, J. Fu, S. Barlow, M. D. Levin, L. Erskine, D. McCord-Maughon, H. Röckel, S. Thayumanavan, S. R. Marder, and J. W. Perry, T. Kogej, D. Beljonne, J.-L. Brédas, M. Albota, S. Hess, C. Xu and W. W. Webb, in "Third-Order Nonlinear Optical Materials" SPIE's International Symposium on Optical Science, Engineering, and Instrumentation; San Diego, CA, (July 19-24, 1998).

J. W. Perry, "Nonlinear Photopolymers and Application to 3-D Microfabrication," Symposium on Optoelectronic Materials for the New Millennium, The Rank Prize Funds, Grasmere, England, (October 12-15, 1998).

J. W. Perry, M. Albota, S. Ananthavel, D. Beljonne, J. L. Bredas, B. Cumpston, D. L. Dyer, J. E. Ehrlich, A. A. Heikal, S. E. Hess, T. Kogej, S. M. Kuebler, I. Y. S. Lee, M. D. Levin, S. R. Marder, D. McCord-Maughon, H. Rockel, M. Rumi, G. Subramaniam, W. W. Webb, X. L Wu, C. Xu, "Design of Organic molecules with Large Two-Photon Absorption Cross Sections," American Chemical Society National Meeting, Anaheim CA, (March 21-25, 1999).

J. W. Perry, "Two-Photon Three-Dimensional Lithography," CLEO-QELS National Meeting, Baltimore, MD, (May 1999).

J. W. Perry, "Conjugated Molecules with Large Two-Photon Cross Sections," ACS National Meeting, New Orleans, LA, (August 1999).

"Three-Dimensional Microfabrication Using Two-Photon Polymerization," B. H. Cumpston, J. E. Ehrlich, S. M. Kuebler, M. Lipson, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, *SPIE Conference on Materials and Device Characterization in Micromachining*, Santa Clara, CA, (September 1998).

W. R. Burghardt, "X-ray Scattering Studies of Molecular Orientation in Liquid Crystalline Polymers under Flow," Texas A&M University, January 28, 2000.

W. R. Burghardt, "Optical and X-ray Probes of Molecular Orientation in Sheared Liquid Crystalline Polymers," Dillon Medal Award Lecture, Paper I2-1, APS March Meeting, Minneapolis, *APS Bulletin* 45(1) 401 (2000).

W. R. Burghardt, "In Situ X-ray Scattering Methods for Studying Polymer Structure Under Flow," in symposium 'Frontiers for Polymer Science in the 21<sup>st</sup> Century' sponsored by ACS Macromolecular Secretariat, ACS National Meeting, San Francisco, March, 2000.

W. R. Burghardt, "In Situ X-ray Scattering Methods for Studying Polymer Structure Under Flow," Chemical Engineering Department, Imperial College, London, August 25, 2000.

V. M. Ugaz and W. R. Burghardt, "In-situ x-ray scattering investigation of the evolution of molecular orientation during transient flows of model thermotropic liquid crystalline polymers," Paper LC1, Society of Rheology National Meeting, Madison, October, 1999.

V. M. Ugaz, W. R. Burghardt, J. A. Kornfield and W. Zhou, "In-Situ X-ray Scattering Investigation of the Evolution of Molecular Orientation During Transient Flows of Model

Thermotropic Liquid Crystalline Polymers," Paper 128a, AIChE National Meeting, Dallas, November, 1999.

N. Vaish, W. R. Burghardt, W. Zhou and J. A. Kornfield, "In situ x-ray scattering study of a main-chain thermotropic liquid crystalline polymer under oscillatory shear flow" Poster L36-62, APS March Meeting, Minneapolis, *APS Bulletin* 45(1) 554 (2000).

J. A. Kornfield, "Nematic Solutions of Large Molecular Side-group Liquid-crystal Polymers," American Chemical Society National Meeting, New Orleans (August 1999).

J. A. Kornfield, "Polymer Solutions and Gels in Nematic Solvents," Society of Rheology Annual Meeting, Madison (October 1999).

W. Zhou, J. A. Kornfield, V. M. Ugaz, N. Vaish and W. R. Burghardt, "Shear orientation and rheology of a main-chain thermotropic LCP: Flow-alignment and orientational flipping in steady and oscillatory shear," Paper LC2, Society of Rheology National Meeting, Madison, October, 1999.

J. A. Kornfield, "Phase Behavior and Dynamics of Nematic Solutions of Side-Group Liquid Crystalline Polymers," American Institute of Chemical Engineers Annual Meeting, Dallas (November 1999).

W. Zhou, W. R. Burghardt, J. A. Kornfield, V. M. Ugaz, N. Vaish, "Shear Orientation and Rheology of a Main-Chain Thermotropic LCP: Flow-alignment and Orientational Flipping in Steady and Oscillatory Shear," Paper 175d, AIChE National Meeting, Dallas, November, 1999.

J. A. Kornfield, W. Zhou, V. M. Ugaz, N. Vaish, W. R. Burghardt, "Oscillatory Shear Alignment and Rheology of a Main-chain Thermotropic Liquid Crystalline Polymer," Paper I2-4, APS March Meeting, Minneapolis, *APS Bulletin* 45(1) 402 (2000).

J. A. Kornfield, "Oscillatory Shear Alignment and Rheology of a Main-chain Thermotropic Liquid Crystalline Polymer," American Physical Society Meeting, Minneapolis (March 2000).

W. Zhou, "Effect of Molecular Weight and Temperature on the Rheological Properties of Thermotropic LCP," Society of Rheology, Columbus (October, 1997)

J. A. Kornfield, "Shear Orientation and Rheology of a Main-chain Thermotropic LCP: Flow-alignment and Orientational Flipping in Steady and Oscillatory shear," poster at the XIIIth International Congress on Rheology, Cambridge, UK (August 2000).

J. A. Kornfield, "Phase Behavior and Dynamics of Nematic Solutions of Side-Group Liquid Crystalline Polymers," poster at the XIIIth International Congress on Rheology, Cambridge, UK (August 2000).

L. Dalton, American Chemical Society National Meeting ICONO'5, Davos, Switzerland.

E. L. Thomas, "Structural Studies of LCPs," CNRS Strasbourg, France June 1999

C. Osuji, "Morphology of Covalent and Hydrogen Bonded Side Group Liquid Crystalline Diblock Copolymers," Ober Ski Hut Seminar, Cornell, January, 2000.

C. Osuji, E.L. Thomas, C. K. Ober, "Morphology of Covalent and Hydrogen Bonded Side Group Liquid Crystalline Dilock Copolymers," American Physical Society, March 2000.

D. Walba, "Design of smectic liquid crystal phases using layer interface clinicity," Invited Lecture for the Symposium on Anisotropic Organic Materials, American Chemical Society 218th National Meeting, New Orleans, Louisiana, August 23, 1999.

D. Walba, "A stable ferroelectric smectic C phase composed of racemic molecules," Invited Lecture for the 7th International Conference on Ferroelectric Liquid Crystals, Darmstadt, Germany, August 31, 1999.

D. Walba, "Ferroelectric Smectic LCs from Racemic Molecules," Invited Lecture for the Symposium for Celebrating the Second Anniversary of the Liquid Crystal Institute, Science University of Tokyo in Yamaguchi, Tokyo, Japan, November 19, 1999.

D. Walba, "Supermolecular Stereochemistry in Liquid Crystals: The First Liquid Conglomerate," University of California, Los Angeles, January 13, 2000.

D. Walba, "Ferroelectric and antiferroelectric bent-core mesogens showing the B7 texture," 18th International Liquid Crystal Conference, Sendai, Japan, July 28, 2000.

D. Walba, "Toward ferroelectric liquid crystal nonlinear optical fibers with a photonic bandgap," SPIE Symposium on Liquid Crystals IV, San Diego, California, August 3, 2000.

C. Ober, MLI/SLO Meeting, Weingarten, Germany, June 3-8, 2000. "Can We Direct Self-Assembly?", *invited talk*.

C. Ober, University of Toronto, Toronto, ON, May 8, 2000. "Directing Complex Polymer Structures via Coupled Interactions", *invited talk*.

C. Ober, Shape Persistent Macromolecules: Chemistry, Physics and Devices, Mainz, Germany, Feb. 28-29, 2000. "The Influence of Shape and Flexibility in Liquid Crystal Block Copolymers", *invited talk*.

C. Ober, Makromolekulares Kolloquium Freiburg, Freiburg, Germany, 24.- 26.2.2000. "Block Copolymers with Liquid Crystalline Segments: the Effect of Architecture on Microstructure and Performance", *invited talk*.

C. Ober, American Chemical Society Meeting, New Orleans, LA, August 22 - 26, 1999. "Mesogen--Jacketed Liquid Crystalline Polymers Via Stable Free Radical Polymerization", "Balancing Liquid Crystallinity With Microphase Separation In Block Copolymers", *invited talk*

P. Palffy-Muhoray, "From Brownian Motors to Lasers: Optical Phenomena in Liquid Crystals", Florida State University, Tallahassee, April 28, 2000.

P. Palffy-Muhoray, "Nonlinear Optics of Liquid Crystals", in SILC Easter School on *Introduction to Theory and Modelling of Thermotropic Liquid Crystals*, Portoroz, Slovenia, April 15-18, 2000.

P. Palffy-Muhoray, "From Brownian Motors to Lasers: Optical Phenomena in Liquid Crystals", Universidad Metropolitan, Mexico City, Mexico, March 1, 2000.

P. Palffy-Muhoray, "Photoalignment of Liquid Crystals", Pontifícia Universidade Católica do Rio de Janeiro (PUC - Rio), Nov. 19, 1999.

P. Palffy-Muhoray, "Ratchets, Brownian Motors and the Photoalignment of Liquid Crystals", University of Sao Paulo, Nov. 17, 1999.

P. Palfy-Muhoray, "Orientational Ratchets in the Photoalignment of Liquid Crystals", Pennsylvania State University, Oct. 29, 1999.

P. Palfy-Muhoray, "Orientational Ratchets in the Photoalignment of Liquid Crystals", Symposium on the Physics of Soft Materials, University of Pennsylvania, Oct. 9, 1999.

P. Palfy-Muhoray, "Lasing in Cholesteric Liquid Crystals", XIII Conference on Liquid Crystals, Krynica Zdroj, Poland, Sept. 13-17, 1999.

P. Palfy-Muhoray, "Dendritic Finger Growth in Hele-Shaw Cells Without Anisotropy", Conference on Pattern Formation in Liquid Crystals, Bayreuth, Germany, Sept. 5-7, 1999.

J. A. Kornfield, "Nematic Solutions of Large Molecular Side-group Liquid-crystal Polymers," American Chemical Society National Meeting, New Orleans (August 1999).

J. A. Kornfield, "Polymer Solutions and Gels in Nematic Solvents," Society of Rheology Annual Meeting, Madison (October 1999).

J. A. Kornfield, "Phase Behavior and Dynamics of Nematic Solutions of Side-Group Liquid Crystalline Polymers," American Institute of Chemical Engineers Annual Meeting, Dallas (November 1999).

J. A. Kornfield, "Phase Behavior and Dynamics of Nematic Solutions of Side-Group Liquid Crystalline Polymers," poster at the XIIIth International Congress on Rheology, Cambridge, UK (August 2000).

J. W. Perry, S. P. Ananthavel, G. Duerksen, J. Ehrlich, A. A. Heikal, K. Mansour, K. Mohanalingam, S. M. Kuebler, H. Röckel, S. R. Marder, T. Kosa, P. Palfy-Muhoray, "Nonlinear Absorption and Two-Photon Charge Carrier Generation in Liquid Crystal Guest-Host Systems", Second International Conference on Optical Power Limiting, Venice Italy, (July 2-5, 2000).

W. R. Burghardt, "In Situ X-ray Scattering Methods for Studying Polymer Structure Under Flow," Physics Department, University of Waterloo, Ontario, October 5, 2000.

W. R. Burghardt, "X-ray Scattering Investigation of Liquid Crystalline Polymer Melts in Complex Channel Flows," Dow Chemical, Midland, MI, October 16, 2000.

W. R. Burghardt, "In Situ X-ray Scattering Methods for Studying Polymer Structure Under Flow," Chemical Engineering Department, California Institute of Technology, Pasadena, CA, October 19, 2000.

W. R. Burghardt, "In Situ X-ray Scattering Methods for Studying Polymer Structure Under Flow," Chemical Engineering Department, Wayne State University, March 2, 2001.

W. R. Burghardt, "In Situ X-ray Scattering Methods for Studying Polymer Structure Under Flow," Materials Science and Engineering Department, Northwestern University, Evanston, IL, October 2, 2001.

W. Burghardt, N. Vaish and D. Cinader, "Molecular orientation in channel flows of main-chain thermotropic LCPs," paper 196g, AIChE National Meeting, Los Angeles, November 2000.

W. Zhou, W. R. Burghardt and J. A. Kornfield, "Shear Aligning Properties of a Main-Chain Thermotropic Liquid Crystalline Polymer," Paper 233g, AIChE National Meeting, Reno, NV, November 2001.

W. R. Burghardt, "Rheo-X-Ray Methods: Exploiting Capabilities of Third Generation Synchrotrons," Paper 128g, AIChE National Meeting, Reno, NV, November 2001.

P. Palffy-Muhoray, "Light Induced Phenomena in Liquid Crystal Elastomers", NASA Glenn Research Center, Cleveland, March 12, 2002.

P. Palffy-Muhoray, "Dynamics of a Light-driven Molecular Motor", Feb. 7, 2002, Dept. of Physics, Wayne State University, Detroit, MI

P. Palffy-Muhoray, "Mirrorless Lasing in Cholesteric Liquid Crystals", Photonics West (Organic Photonic Materials and Devices IV), Jan. 20-25, 2002, San Jose.

P. Palffy-Muhoray, "Lasing in Liquid Crystal Elastomers", Naval Research Lab., Dec. 5, 2001, Washington, D.C.

P. Palffy-Muhoray, "Lasing in Liquid Crystal Elastomers", Fall Meeting of the Materials Research Society, Nov. 26-30, 2001, Boston.

P. Palffy-Muhoray, "Mirrorless Lasing in Cholesteric Liquid Crystals", Dept. of Physics, Simon Fraser University, Burnaby, BC, Canada, Nov. 21, 2001

P. Palffy-Muhoray, "Mirrorless Lasing and Laser-like Emission in Liquid Crystals" Symposium on Organic Electronic and Photonic Materials, Tokyo Institute of Technology, Osaka, Oct. 31, Nov. 2, 2001

P. Palffy-Muhoray, "Nonlinear Optics of Liquid Crystals", 5th Ibero-American Conference, Maringa, Brazil, Sept. 2-5, 2001.

P. Palffy-Muhoray, "Dynamics of a Light-driven Molecular Motor", First International Conference on Applied Statistical Physics: Molecular Engineering: ASTAPHYS-MEX-2001, Cancun, Mexico, July 23-27, 2001

P. Palffy-Muhoray, "From Brownian Motors to Lasers: Dyes at Work in Liquid Crystals", University of Texas at El Paso, Feb. 16, 2001

P. Palffy-Muhoray, "From Brownian Motors to Lasers: Dyes at Work in Liquid Crystals", Tokyo Institute of Technology, Nov. 21, 2000.

"Physics Of Thresholdless Switching In Tilted Chiral Smectics," N.A. Clark, D. Coleman, and J.E. MacLennan, *18<sup>th</sup> International Liquid Crystal Conference, Sendai, Japan* (2000).

"Field-Controlled Surface Electroclinic Effect In Chiral SmecticS," R. Shao, D. Muller, N.A. Clark, D.M. Walba, and J.E. MacLennan, *18<sup>th</sup> International Liquid Crystal Conference, Sendai, Japan* (2000).

"Total Internal Reflection Study Of Azimuthal Anchoring Of W415," D. Coleman, G. Danner, and N.A. Clark, *18<sup>th</sup> International Liquid Crystal Conference, Sendai, Japan* (2000).

"Transition Between Antiferroelectric And Ferroelectric Order At The Lc-Solid Interface," D. Coleman, S. Bardon, L. Radzihovsky, G. Danner, And N.A. Clark, *18<sup>th</sup> International Liquid Crystal Conference, Sendai, Japan* (2000).

"Liquid Crystals In SiO<sub>2</sub> Opals," D. Kang, J.E. MacLennan, N.A. Clark, and R.H. Baughman, *18<sup>th</sup> International Liquid Crystal Conference, Sendai, Japan* (2000).

"Polarity-Controlled Double-Layer Formation In Ferroelectric Liquid Crystal Cells: Electrical And Electro-Optic Behavior," G. Strangi, J.E. Maclennan, and N.A. Clark, *18<sup>th</sup> International Liquid Crystal Conference, Sendai, Japan* (2000).

"Bistability, Monostability, 'V-Shaped' Response, And The Influence Of Ions In Ferroelectric Liquid Crystal Cells," M. Copic, J.E. Maclennan, and N.A. Clark, *18<sup>th</sup> International Liquid Crystal Conference, Sendai, Japan* (2000).

"V-Shaped Switching In Chiral Smectics," P. Rudquist, S.T. Lagerwall, N.A. Clark, J.E. Maclennan, R. Shao, D.A. Coleman, S. Bardon, D.R. Link, T. Bellini, and D.M. Walba, *18<sup>th</sup> International Liquid Crystal Conference, Sendai, Japan* (2000).

"Domain Switching In Achiral Smectic C Liquid Crystals," C. Jones, R. Shao, and N.A. Clark, *Bulletin of the American Physical Society*, **46**, 689 (2001).

"Self-Assembly In Lyotropic Chromonic Liquid Crystals," P.K. Maiti, Y. Lansac, M.A. Glaser, and N.A. Clark, *Bulletin of the American Physical Society*, **46**, 691 (2001).

"Rapid Formation Of Colloidal Photonic Crystals," D. Kang, S.B. Nagel, J.E. Maclennan, and N.A. Clark, *Bulletin of the American Physical Society*, **46**, 809 (2001).

"Behavior Of Liquid Crystals In The Smectic A Phase On Periodically Patterned Isotropic Surfaces," C. Lemke, and N.A. Clark, *6<sup>th</sup> European Conference on Liquid Crystals, Halle (Saale), Germany* (2001).

"Structure And Dynamics Of Ferroelectric Liquid Crystal Cells Exhibiting Threshold-Less Switching," M. Copic, J.E. Maclennan, and N.A. Clark, *8<sup>th</sup> International Conference on Ferroelectric Liquid Crystals, Washington DC*, (2001).

"Enhancement Of Surface Electro-Clincic Effect Magnitude By Addition Of A Layer Swelling Dopant," D.A. Coleman, J. Fish, and N.A. Clark, *8<sup>th</sup> International Conference on Ferroelectric Liquid Crystals, Washington DC*, (2001).

"Domain Nucleation And Switching Behavior In Achiral Smectic C Liquid Crystals," C.D. Jones, R. Shao, J.E. Maclennan, and N.A. Clark, *8<sup>th</sup> International Conference on Ferroelectric Liquid Crystals, Washington DC*, (2001).

"Unusual Thickness-Dependent Thermal Behavior And Anticlinic Coupling In Chiral Smectic Free-Standing Liquid-Crystal Films," P.J. Wu, C.R. Lo, T.C. Pan, D.R. Link, J.E. Maclennan, N.A. Clark, M. Veum, C.C. Huang, and C.Y. Chao, *8<sup>th</sup> International Conference on Ferroelectric Liquid Crystals, Washington DC*, (2001).

"Alignment On Photobuffed Surfaces And On Photopatterned Self-Assembled Monolayers," Alignment Workshop, Ferroelectrtic Liquid Crystal Materials Research Center, Boulder, CO, *Invited talk*, (2000).

"Application Of Ferroelectric LCDs," 2000 Invited International Seminar Program, Korean Liquid Crystal Society, Seoul, Korea, *Invited talk* (2000).

"Polarity And Chirality In Liquid Crystals: Novel Phases, Structures, And Electro-Optics," Eighth International Conference on Ferroelectric Liquid Crystals, Washington, D.C., *Invited talk* (2001).

### New Discoveries/Inventions/Patents

**S.-T. Wu and S. Marder:** Joint invention disclosure on high dielectric anisotropy nematics.

**J. Kornfield:** "Polymers for Control of Orientation and Stability of Liquid Crystals" (provisional patent filed 4/99).

**S. Marder:** "Hole-transporting Polymers," Patent Application No. 60/083,260 (filed 4/27/98).

**L. Dalton:** "Polar Tolane Liquid Crystals" submitted by HRL.

**P. Palffy-Muhoray:** "Waveguide Based Cholesteric Display."

**S.-T. Wu, S. Marder, and Q. Zhang:** "Dopants for Liquid-Crystal Devices" (US Patent filed April 2, 1999).

**S.-T. Wu, S. Marder, Q. Zhang:** "Colorless High Dielectric Compounds" (US Patent filed April 2, 1999).

**S. Marder, J. Perry, W. Zhou, S. Kuebler, and J. Cammack:** "Materials, Methods, and Uses for Photochemical Generation of Acids (and/or Radical Species)" (provisional patent filed (UA01-078) 28 March 2002).

## **Honors and Awards**

### **Burghardt:**

NSF Young Investigator Award, 1993.  
Colburn Lecturer, University of Delaware, 1997.  
John Dillon Medal, American Physical Society, March 2000.

### **Clark:**

Fellow of the American Association for the Advancement of Science, 1999.

### **Dalton:**

Distinguished Alumni Award of Michigan State University, 2000.

### **Kornfield:**

NSF Young Investigator Award, 1990.  
Emerging Scholar Award of the American Association of University Women, 1993.  
Associated Students of Caltech Teaching Award, 1994.  
John Dillon Medal, American Physical Society, March 1996.  
Colburn Lecturer, University of Delaware, 1998.  
Fellow of the American Physical Society, March 2000.

### **Marder:**

Member Board of Reviewing Editors, Science Magazine.  
Special Creativity Award, National Science Foundation, 1997 (with **J. Perry**).

### **Ober:**

Humboldt Fellowship, 1993.  
Special Creativity Award, National Science Foundation, 1997.  
Winner of the 2000 SRC/SSA/International Sematech (ISMT) Award for research in manufacturing and environment, safety and health with Gina Weibel, a Cornell MS&E graduate student, and Karen K. Gleason and Hilton G. Pryce-Lewis of MIT.

### **Perry:**

Special Creativity Award, National Science Foundation, 1997 (with **S. Marder**).

### **Thomas:**

Polymer Physics Prize, American Physical Society, 1991.  
Fellow of the American Physical Society, 1986.  
Creative Polymer Chemist Award, American Chemical Society, 1985.  
Special Creativity Award, National Science Foundation, 1988 and 1996.

### **Walba:**

Fellow of the American Association for the Advancement of Science, 1999.